ADDITION OF TRANSITION ELEMENTS TO THE PHOSPHATE SEALING OF CERIUM OXIDE PROTECTIVE PRIMER DEPOSITED ON AA2024-T3 ALLOY

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ABSTRACT

A concise investigation was undertaken to determine the impact of transitional elements on the phosphate sealing of cerium oxide primer layers deposited on AA2024-T3 aircraft alloy. The cerium oxide primer layers were deposited electrochemically on preliminary treated alloy specimens under potentiostatic conditions. The subsequent phosphate sealing layer deposition was performed in equimolar solutions of NaMoO₄, NaVO₃, or ZrO(NO₃)₂ in (NH₄)₂HPO₄ medium for 30 min at 90°C. The already coated and sealed specimens were submitted to comparative measurements via electrochemical impedance spectroscopy and linear voltammetry after 168 h of exposure to 3.5% NaCl model corrosive medium. The obtained bi-layer coatings were characterized by systematic analyses using scanning electron microscopy, energy dispersion X-ray spectroscopy and X-ray photoelectron spectroscopy. The latter analysis evinced that cerium present in a cerium phosphate coating was predominantly in Ce(III) state, while doping by Mo, V and Zr caused oxidation to Ce(IV) species. The results obtained reveal successful inclusion of these elements inside the phosphate sealing layer.

Keywords: aircraft alloys, Cerium Oxide Primer Layers (CeOPL), phosphate sealing, transition elements.

INTRODUCTION

The industrial aluminum alloys possess exactly defined chemical compositions and structural features corresponding to the respective industrial standards. Nevertheless, additive elements form precipitate inclusions, which in turn bring about the so called “undesirable voltaic elements” [1] interrupting the native surface oxide layer of the aluminum matrix and thus causing detrimental surface effects. AA2024 alloy is a susceptible material in this respect, as it contains about 4 % copper and 1.2 % Mg. The presence of these elements provides the transformation of the interfaces into pitting initiation centers. Then pitting changes to intergranular corrosion decreasing the effective cross-sectional area and the mechanical strength of the metallic details, assemblies and constructions [2]. Therefore the surface coating deposition is an indispensable procedure for efficient corrosion protection of various metallic products. In industry it is commonly accepted to deposit multilayered coating systems [3], where each layer has its own specific function. In this sense, the primer layers enhance the adhesion between the metallic substrate and the upper coating layers. Phosphatation is one of the most common primer layer deposition approaches. Various recipes for this procedure can be found in the literature [4 - 7].
Recently, Heller et al. [8] have proposed this procedure for sealing of cerium oxide primer layers deposited on aircraft alloys. Another approach to primer coatings deposition refers to the application of transitional elements, such as vanadium and molybdenum as proposed by Voevodin et al. [9]. Besides, electrodeposition has evinced as an efficient method for cerium oxide layer deposition [10 - 13].

All facts mentioned above have predetermined the aim of the present research work, namely to evaluate the possibility to involve transitional elements inside the phosphating sealing of cerium oxide primer layer deposited on AA2024-T3 aircraft alloy.

EXPERIMENTAL

30 x 30 x 3 mm AA2024-T3 plates were submitted to a sequence of procedures related to preliminary treatment, cerium oxide layer deposition and final phosphatic sealing.

Preliminary treatment procedure: all metallic plates were submitted to alkaline etching in NaOH aqueous solution (50 g dm⁻³) for 2 min at 50ºC followed by 10 min immersion in HNO₃ aqueous (1:1) solution at room temperature.

Cerium oxide primer layers (CeOPL) cathodic deposition procedure: the preliminary treated specimens were submitted to an electrochemical deposition of cerium primer layers. This procedure was performed in correspondence with the best results reached so far [10, 12, 13]. It included cathodic deposition at -1V measured vs. Ag/AgCl reference electrode (potential values subsequently cited in the text refer to this reference electrode) for 360 s at room temperature. The depositions were carried out in 100 ml of 0.03 M (NH₄)₂Ce(NO₃)₅ aqueous solution with addition of 0.7 ml 30 % aqueous solution of H₂O₂ as a deposition activator. The exposed surface area was circular with a diameter of 23.5 mm.

Phosphate sealing procedure: phosphate sealing procedure was carried out to evaluate the influence of the transition elements on the performance of the investigated alloy. It proceeded for 30 min at 90ºC in already heated phosphate solutions. Their compositions are shown in Table 1.

Electrochemical measurements: a comparative assessment was executed after 168 hours of exposition to a model corrosive medium (3.5 % NaCl aqueous solution). This approach provided better outlining of the barrier capability of the coatings after an entire week of exposition to the model corrosive medium. Both the cathodic deposition and the electrochemical characterization procedures were performed by a potentiostat-galvanostat “Autolab 30” with Frequency Response Analyser “FRA-2”. The electrochemical measurements included electrochemical impedance spectroscopy (EIS), followed by linear voltammetry. The EIS spectra were acquired in the frequency range from 10⁴ Hz to 10⁻² Hz in respect to the open circuit potential (OCP). Its values were determined immediately prior to the respective spectrum acquisition, i.e. 30 s after cell connection. The perturbation signal was ±30 mV in respect to the open circuit potention (OCP). The subsequent voltammetric measurements were performed by acquisition of separate cathodic and anodic curves. The cathodic curves were recorded in the range from +30 mV to -500 mV at a potential sweep rate of 1 mV s⁻¹. The anodic curves were obtained after the restoration of the original OCP value deviated by the polarization resulting from the cathodic curve acquisition. A larger potential range was

<table>
<thead>
<tr>
<th>Solution code</th>
<th>Basic ingredient</th>
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<tr>
<td></td>
<td>Formula</td>
<td>Concentration</td>
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<tr>
<td>REF</td>
<td>(NH₄)₂HPO₄</td>
<td>0.03 mol dm⁻³</td>
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<tr>
<td>Mo</td>
<td>(NH₄)₂HPO₄</td>
<td>0.03 mol dm⁻³</td>
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<tr>
<td>V</td>
<td>(NH₄)₂HPO₄</td>
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<tr>
<td>Zr</td>
<td>(NH₄)₂HPO₄</td>
<td>0.03 mol dm⁻³</td>
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*The calculations of its concentration are done on the basis of the molecular mass of the dry compound.
selected in order to observe the entire passivity region. It was between -30 mV and +700 mV. The same potential sweep rate was used.

**Surface characterization methods:** the morphology, the surface composition and the element distribution were observed by scanning electron microscopy (SEM), combined with energy dispersive X-ray (EDX) spectroscopy. TESCAN (SEM/FIB LYRA I XMU) was used. The EDX map analysis was performed with a Bruker detector attached to the microscope.

X-ray photoelectron spectroscopy (XPS) was used for investigation of the surface of cerium phosphate coating on AA2024-T3 type alloy doped by different elements (Mo, V, Zr) prior to and after the corrosion test performed. XPS analyses were carried out on Kratos AXIS Supra with a monochromatic Al X-ray source. Each analysis started with a survey scan from 0 eV to 1200 eV. One sweep of pass energy of 160 eV was applied at steps of 1 eV. Higher resolution was achieved by increasing the number of sweeps and decreasing the pass energy to 20 eV as well as the steps to 100 meV. Lines corresponding to C1s, O1s, Al2p, Ce3d, Na1s, N1s, P2p and the doping elements present were recorded and the spectra obtained were discussed. The O1s peak fitting was performed by XPS PEAK 4.1 software. The Gaussian - Lorentzian product function was used to describe the O1s component peaks.

**RESULTS AND DISCUSSION**

**In situ chronoamperometric curves:** the chronoamperometric curves acquired during CeOPL electrodeposition indicate relatively low repeatability. This is due to the random distribution of the intermetallics on the alloy’s surface. It is well known that AA2024 alloys have a high content of copper and magnesium which form various intermetallic precipitates. Consequently, although the entire surface is electrically charged (i.e. a value of -1 V is reached), the electrochemical CeOPL deposition proceeds predominantly on the areas occupied by the intermetallic inclusions, where the native Al-oxide layer is interrupted. Fig. 1 shows that the initial decay of the current density probably due to electric double layer charging is followed by an increase until a maximum marked by line “A” is outlined. The current density increase is attributed to consumption of electric charges, which in turn is related to hydrogen evolution because of the well expressed acidic character of the pentanitrocerate solutions used [14, 15].

According to the theoretical grounds of CeOPL deposition described in the literature [15, 16], this reaction coincides with island-like coating nucleation on the most active domains of the alloy. Thus, the locations of the most active zones, occupied by S-phase Al2 (Cu,Mg)

![Fig. 1. In-situ chronoamperometric curves acquired during the CeOPL deposition.](image-url)
and θ-phase, composed by Al₂Cu [18,19] become centers of preferential CeOPL deposition. As these centers are already covered by Ce-oxides/hydroxides and/or H₂ gas bubbles, subsequent current decrease is observed. It is followed by a second peak, marked by line “B”, corresponding to localized preferential island-like nucleation on the less active finer intermetallic inclusions such as (Al, Cu)(Fe, Mn)ySi described elsewhere [20]. Another factor, influencing the curve shape during CeOPL deposition is the distribution of the basic Al-matrix grains during the post treatment [21, 22], which predetermines the intermetallic inclusions re-distribution, described above (i.e. the larger the average size of the basic Al-matrix grains is, the greater the distances between the intermetallics are). In view of all comments pointed above, it can be concluded that AA2024 samples, selected for deposition, show deviations from the nominal composition due to the random intermetallic distribution. The sample selected for Mo-containing phosphate application has the highest intermetallic content, whereas the plate used for the referent phosphate finishing layer has the lowest quantity of intermetallics. It is worth adding that the composition of the remaining two plates corresponds to the nominal AA2024 composition. Regardless of the deviations observed among the deposition curves, they all overlap almost completely within the final deposition stage (i.e. after 350 s) at a current density of 6 mA cm⁻². This fact evidences that the deposition procedure is completed within 5 min, which enables to overcome the inconveniences related to the alloys’ compositional heterogeneity.

Electrochemical characterizations: the electrochemical characterization performed after 168 h of exposition to a model corrosive medium composed of 3.5 % NaCl aqueous solution shows a negligible effect of the dopants used on the protective capabilities of CeOPL layers. The impedance spectra shown in Fig. 2 overlap almost completely and correspond to that of a corroding bare metal. The phase angle in the frequency range between 10 kHz and 1 kHz is almost zero, which indicates that the coatings do not possess efficient barrier ability and the electrolyte can freely access the metallic surface. There is a time constant (RC-unit) in the middle frequency range which is related to the charge transfer resistance, Rct. The latter refers to all electrochemical reactions of the overall corrosion process and the constant phase element Qedl+oxy attributed to the capacitance of both the electrical double layer and Al native oxide layer. The total impedance at 10 mHz reaches a value of almost 10⁴ Ω cm⁻², which is typical for the polarization resistance of a corroding bare metal.

The results obtained are in complete accordance with the polarization measurements presented in Fig. 3. In accordance with the impedance spectra, all cathodic curves (Fig. 3a) almost coincide. There are sharp current drops at -1 V and at -1.250 V for Mo and V-doped coatings, correspondingly. They are probably related to the following transitions:

![Fig. 2. Nyquist (a) and Bode (b) plots of EIS spectra acquired after 168 hours of exposition of the investigated specimens in the model corrosive medium.](image-url)
Mo(V) + 2e⁻ → Mo(III)  \hspace{1cm} (1)
V(V) + 2e⁻ → V(III)  \hspace{1cm} (2)

The anodic curves show short passivity plateaus for the referent and Mo doped specimens. They are attributed to the so called “strength against pitting nucleation” [22] and reveal higher resistance against localized corrosion attack. But this resistance is negligible and does not significantly affect the corrosion processes taking place on the metallic surface. In fact, the polarization resistance of the specimens is of the order of the values obtained for the corroding bare metal, i.e. between 6 kΩ cm⁻² and 7 kΩ cm⁻².

Morphological observations: SEM/EDX analyses (Fig. 4) show successful incorporation of the elements investigated inside the phosphate sealing layers. As it can be seen from the figure, they are uniformly distributed on the entire surface. However, their amounts seem to be rather low. One of the obvious reasons for this fact refers probably to the low thickness of the phosphate sealing layer, which in this case serves as an additive element provider.

Surface compositional investigations: Ce3d, P2p, as well as O1s photoelectron lines of the coatings investigated prior to the corrosion tests are presented in Fig. 5. According to O1s and Ce3d spectra the surfaces of the examined coatings are oxidized. The oxidation state of the constituent elements is evaluated on the ground of the spectra fitting procedure described above. The first peak is recorded at ca 529.5 eV and is associated to Ce-O bonds in the lattice of CeO₂ [23]. The second peak at 531.2 eV refers to the oxygen in CePO₄ [24], while the third peak at 532.5 eV is attributed to the oxygen in Ce-OH. In case of Zr doping an additional photoelectron peak appears, which most probably is due to the presence of water on the surface. Here, it is worth mentioning that the most intensive peak is that at 531.2 eV, which means that CePO₄ is formed on the film surfaces [25]. The P2p photoelectron line for all investigated coatings is registered at 133.3 eV, a value typical for the phosphorus in CePO₄ compound [24]. Besides, the existence of P₂O₅ is also possible, because the coatings are not thermally treated.

The photoelectron spectra of Mo, V and Zr used as doping elements are not shown here. The binding energies of Mo3d, V2p as well as Zr3d are typical for the oxidation state of these elements. Small amounts of Al in an oxidized form are most probably detected because the deposited oxide films are very thin as a result of the short deposition time used (360 s) or their poor adhesion to the substrate. The Ce3d spectra are complex as a result of the spin-orbital splitting into a doublet and each of them shows extra structures due to final state effects [26]. All data considered above leads to the conclusion that cerium in pure cerium phosphate coating is predominantly in Ce³⁺ state. The doping by B, Mo, Ni, Si, V, Zr and Zn brings about its oxidation to Ce⁴⁺.

The amount of Ce⁴⁺ in the oxide films is evaluated...
Fig. 4. SEM/EDX images of the deposited coatings (a - reference composition, b - composition with addition of NaMoO$_4$, c - addition of NaVO$_3$, d - addition of ZrO(NO$_3$)$_2$).
as a percentage of the area of uIII peak at ca 916.8 eV in respect to the total Ce3d peak area. It is found that it varies from 0 % to 14 %, while Ce (IV) percentage to total amount of Ce varies from 0 % to 100 % [24]. The values obtained are shown in Table 2. CeOPL phosphatation results in inhibition of Ce(IV) reducibility. It is better expressed in the case of Zr doped specimen.

It is suggested that some of Ce(III) detected by XPS originates from CePO$_4$ film, which covers that of cerium oxide already electrochemically deposited. It is worth noting that the decrease of Ce(III), and hence the increase of Ce(IV) in CePO$_4$/CeO$_2$-Ce$_2$O$_3$ oxide films corresponds to the change in the form of the polarization curves discussed. This means that the corrosion of the samples doped by Mo, V and Zr starts after CePO$_4$ removal by the aggressive medium. Since this compound is almost insoluble in aqueous media [27], its removal results most likely from leaching. The latter is attributed to initial corrosive dissolution of the underlying nonstoichiometric cerium oxide, followed by that of the metallic substrate.

The theoretical consideration of Ce-oxide deposition [16, 17] treats the oxidation of Ce(III) to Ce(IV) as an indispensable intermediate stage. In fact, the mechanism proposed by Aldykiewicz et al. [16] and illustrated by Lau et al. [17] suggests several simultaneously proceeding stages of CeOPL deposition:

• formation of intermediated complex species:
  \[ 2\text{Ce}^{3+aq.} + \text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow \text{Ce(OH)}_2^{2+aq.} \]  \tag{3}  
• a reaction of the obtained complex ions with hydroxyl ions near the metallic surface:
  \[ \text{Ce(OH)}_2^{2+aq.} + 2\text{OH}^- \rightarrow \text{Ce(OH)}_3^+ \rightarrow \text{CeO}_2 + 2\text{H}_2\text{O} \]  \tag{4}  
• a subsequent conversion of cerium hydroxides to the respective oxides:
  \[ \text{Ce(OH)}_4 \rightarrow \text{CeO}_2 + 2\text{H}_2\text{O} \]  \tag{5}  

Lau et al. [17] even propose the presence of CeO$_3$(OH)$_2$ as a complex intermediate product, which converts to CeO$_2$. Furthermore, the deposited cerium oxide reacts readily with oxygen from the ambient environment. In view of these concepts it can be inferred that the subsequent phosphatation by (NH$_4$)$_2$HPO$_4$ leads to reduction of some of Ce(IV) oxides/hydroxides, while the presence of other transitional elements such as Mo, V or Zr hinders this process.

Different schemes describing the effect of CePO$_4$ on the kinetics of cerium oxide reduction can be advanced on the ground of the widely accepted mechanisms of Ce(IV) reduction to Ce(III) [28]. They refer to H activation, formation of new OH- groups at the surface of cerium oxide (a reversible reduction), water adsorption and desorption, and a surface O-vacancy formation (an irreversible reduction). The presence of CePO$_4$ can influence the reduction of Ce oxide surface because O$^2-$ diffusion from the coated (by cerium oxide) bulk to the surface is inhibited by its presence in the surface/subsurface region. Besides, the presence of CePO$_4$ reduces the effective area of O diffusion from the bulk to the surface. This in turn decreases the rate of the surface reduction process. The possibility that some of P can migrate into the inner bulk of Ce oxide cannot be ruled out as a result of the presence of CePO$_4$ on the surface of the films studied. Phosphorus in the inner layers may deteriorate the bulk O$_2^-$ diffusion properties and, hence, both the reducibility and the oxygen storage capacity properties of Ce oxides. It is reported that P(V) ions can enter the fluorite CeO$_2$ structure and although their solubility amounts to only a few percent of P$_2$O$_5$, the substitution of Ce(IV) with P(V) results in a reduction
of O-vacancy population [29].

X-ray photoelectron spectroscopy investigation is repeated for the same group of samples after 168 h of exposition to the model corrosive medium. Unfortunately, cerium, phosphorus as well as Mo, V and Zr doping elements are not detected on the surface. Only Al\(^{3+}\), Cu\(^{2+}\) and Mg\(^{2+}\) ions are found present in addition to Cl\(^{-}\) and Na\(^{+}\) from the corrosive medium used.

Fig. 5. Ce3d, P2p and O1s photoelectron spectra of the investigated specimens.
CONCLUSIONS

Following the recent trends in the field of elaboration of alternative environmentally friendly primer layers deposition and subsequent sealing, several transition elements alternative to the toxic Cr(VI) were successfully incorporated in the phosphate sealing thin layers applied to the respective cerium oxide primer layers on AA2024-T3 aircraft alloy. The electrochemical measurements carried out after 168 h of exposition to the model corrosive medium showed a typical behavior of a corroding bare metal, i.e. the sealed coatings investigated revealed unsatisfying protective capabilities.

The analytical techniques used showed that doping by Mo, V and Zr lead to oxidation of the predominantly present Ce(III) species irrespectively of these elements low content. Most probably they hindered Ce(IV) ions reduction during the phosphatation procedure and thus hampered the corrosion protection of the aircraft aluminum alloy studied.

Further experiments in presence of a higher content of the doping elements pointed above are planned.

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REFERENCES


