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Influence of the deposition conditions on the properties of D16 AM clad alloy, dip-coated in Ce-containing baths

D. S. Rodríguez[1], S. Kozhukharov [2]*, M. Machkova [2], V. Kozhukharov[2]

[1]*University of Vigo, Lagoas, Marcosende 36310 (Spain)*

[2]*University of Chemical Technology and Metallurgy, 8 "Kl. Okhridsky" blvd., Sofia 1756 (Bulgaria)*

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The aim of the present research work is to elucidate the influence of various conditions on the spontaneous deposition of cerium conversion layers from solutions of diammonium pentanitrocerate $(NH_4)_2Ce(NO_3)_5$ on D16 AM clad alloy, via dip-coating, and to perform posterior comparative analysis on both the performance and features of the obtained coatings. Their characterizations are done by means of durability tests in a model corrosive medium, composed by 3.5% NaCl solution, combined by regular electrochemical measurements, and subsequent morphological characterizations. The former were executed by Electrochemical Impedance spectroscopy (EIS) coupled by Linear Sweep Voltammetry (LSV), whereas the latter were performed by Scanning Electron Microscopy (SEM), combined by Energy Dispersive X-ray Analysis (EDX). As a result, the optimal conditions for deposition of cerium conversion layers via dip-coatings are determined.

Key words: Aluminium alloy, corrosion, EIS, LSV, SEM, EDS

INTRODUCTION

The metal alloys encounter extreme importance for all kinds of aircraft, automobile, railway, pipeline and marine transport. Nevertheless, they always possess considerable aptitude to suffer corrosion. On the other hand, the recent environmental restrictions [1 - 4], emerge the application of environmentally friendly compounds for coating depositions. In that means, intensive research activities for application of Ce-compounds as corrosion inhibitors or coating ingredients on steels [5 – 9], aluminium [10 - 15] or magnesium [16, 17] alloys have been undertaken. The real coating systems are multilayered, and each layer has its own function, contributing to the entire coating system [18 – 20].

In that means, the Cerium Conversion Coatings (CeCC) can serve as an excellent base for primer and finishing layers, providing better adherence of the upper layers, and active corrosion protection via "self healing" effect [21, 22]. Arenas describes the conversion coatings as products of chemical or electrochemical process, consisted on formation of a metallic oxide, with different properties, being substitute of the native superficial oxide layer of the respective substrate [22]. Undoubtedly, the features and performance of the CeCC are predetermined by the metallic surface prior to deposition, as well as the deposition conditions. Conde et al. [23] remark that the obtaining of desirable covering layer passes through chemisorption processes on the superficial oxide layer of the aluminum that could be described in brief, as follows:

$$-\mathrm{Al{-}OH_2}^{+} \leftrightarrow -\mathrm{AlOH} + \mathrm{H}^{+} \qquad (1)$$

$$-\mathrm{Al{-}OH} + \mathrm{Ce}^{3+} \leftrightarrow [-\mathrm{Al{-}O}\cdots\mathrm{Ce(III)}]^{2+} + 2\mathrm{H}^{+} \qquad (2)$$

According to them, this chemisorption process passes via formation of intermediated complexes on the metallic surface, such as: $Al–O-Ce-(OH)_2^{2+}$. This intermediate process is crucial for the formation of adherent protective film instead of colloidal precipitates and sediments in the solution.

Taking into account that the superficial oxide layer of the aluminum consists simultaneously on: Al_2O_3, $Al(OH)_3$ and $AlO(OH)$ phases [24], it could be assumed that the composition of the oxide layer has extreme importance for the formation of well defined adherent protective layer, instead of precipitates and sediments. The oxide layer as structure and composition depends so on the preliminary treatment applied, so on the pH of the medium during the deposition.

Besides the metallic superficial composition and roughness, the Al-oxide layer composition, the bulk and localized solution pH, concentrations of reactants, products and additives, reaction time and

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* To whom all correspondence should be sent:
E-mail: stephko1980@abv.bg

temperature, are some of the more important parameters that must be controlled [21].

The aim of the present research activities is to follow the correlations between several important parameters of CeCC deposition and combinations of them on the features of the respective coatings, and their performance in a model corrosive medium

EXPERIMENTAL

Metallic substrates

Clad alloy D16 AM, classified by GOST 172342-99 [25] delivered by Klöckner Metalsnab (Bulgaria) was used as a substrate material. According to the standard, this aluminium alloy contains: Cu, 3.8 – 4.9 $\%_{wt}$; Mg, 1.2 – 1.8$\%_{wt}$; Fe 0.5$\%_{wt}$, Si 0.5 $\%_{wt}$, Mn 0.3 – 0.9 $\%_{wt}$, Zn 0.25 $\%_{wt}$, Ti – up to 0.15$\%_{wt,}$ Cr – up to 0.10$\%_{wt}$ as alloying elements. Five coupons with equal sizes of 40x40x4 mm have passed different treatments and subsequent depositions.

Preliminary treatments

All the substrates have passed preliminary superficial treatment, either by only mechanical, or combined with alkaline etching and acidic activation, according to the following procedures:

- *Mechanical grinding:* All of the samples underwent mechanical treatment. It was performed by subsequent grinding with: 250, 500, 800 and 1000 grit SiC emery papers, followed by cleaning with tap – and distilled water.

- *Alkaline etching:* The chemical treatment was executed by etching in 50 g/l. NaOH aqueous solution for 2 minutes at 55 °C. Afterwards, the plates passed vigorous cleaning by tap and distilled water. Finally, the samples have passed acidic activation in HNO_3: H_2O (1:1) for 10 minutes at ambient temperature. After each stage of preliminary treatment, the plates passed vigorous cleaning by tap and distilled water.

Deposition conditions:

The deposition procedures were performed by dip-coating for 2 hours into the respective coating solutions at 55 ˚C in thermostat. All of the coating solutions contained $(NH_4)_2Ce(NO_3)_5$, NaCl, H_2O_2 in distilled water. For the purpose of the investigation, the respective ingredients had different concentrations. Only the NaCl was always added to be 35 g. per liter of the coating solution. The compositions of the solutions and the preliminary treatments are ordered in Table 1. Taking into account the extreme importance of pH of the coating solution, it was maintained by Lourier buffer [26]. It was prepared by mixing of two initial solutions in appropriated relation. Solution 1 was obtained by dilution of 8.5 ml of 36% HCl, up-to 1000 ml. Solution 2 was prepared by dissolving of 7.5 g. glycine and 5.85 g. NaCl in 1000ml. of distilled water. The final buffer solution was obtained by addition of 600 ml of solution 2 to 400 ml. of solution 1, in measuring flask.

Measurements and characterization

Electrochemical measurements - A three-electrode electrochemical flat cells with 100 ml. of 3.5%wt. NaCl solution were used for all electrochemical measurements. Circular section (area equal to 2 cm^2) from each sample surface was selected as a working electrode (WE). The counter electrode (CE) was a platinum net with two orders of magnitude larger area than that of the working electrode in order to avoid the influence of its surface capacitance on the experimental results. All WE-potential values were measured versus a commercial Ag/AgCl – 3M KCl, referent electrode, model 0726100, produced by Metrohm, with potential $E(Ag+/AgCl) = 0.2224$ V. The polarization and impedance measurements were carried out by means of a potentiostat/galvanostat AUTOLAB PG 30/2 of ECOCHEMIE, Netherlands, supported by a frequency response analyzer FRA-2. In order to avoid the influence of the external static electric fields, the electrochemical cell was inserted in a Faraday cage.

- Electrochemical impedance spectroscopy: Frequency range: between 10^4 and 10^{-2} Hz, distributed in 7 steps per decade, at signal amplitude: 10 mV vs. OCP.
- Cathodic polarization curves - in range: from (OCP -500 mV), to (OCP + 10mV) with potential sweep range: 1mV/s.
- Anodic polarization curves - in range: from (OCP -10 mV), to (OCP + 500mV) with potential sweep range: 1mV/s.
- *Surface observation* – The observations via SEM were executed only on the best samples (e.g: these specimens, that showed the highest barrier abilities) using Scanning Electron Microscopy (SEM), (TESCAN, SEM/FIB LYRA I XMU). The SEM observations were combined by Energy Dispersion X-Ray Spectroscopy (EDS), performed by E, (Quantax 200 of BRUKER detector), connected to the SEM-device.

RESULTTS AND DISCUSSION

Comparison of the impedance spectra:

Fig. 1 represents three impedance spectra in Bode (a) and Nyquist (b) plots of the first three samples, coated either in solutions with different

Table 1. CeCC coatings and conditions of their preparations

Sample	Basic compound	Concentration (M)	pH	Presence of buffer	Quantity of H_2O_2 (ml / l)	Preliminary treatment
P1	$(NH_4)_2Ce(NO_3)_5$	0.10	2.00	+	25	Only mechanical
P2	$(NH_4)_2Ce(NO_3)_5$	0.10	2.00	+	25	Mechanical and alkaline
P3	$(NH_4)_2Ce(NO_3)_5$	0.05	2.00	-	25	Mechanical and alkaline
P4	$(NH_4)_2Ce(NO_3)_5$	0.05	2.61	-	25	Mechanical and alkaline
P5	$(NH_4)_2Ce(NO_3)_5$	0.10	2.00	+	50	Only mechanical

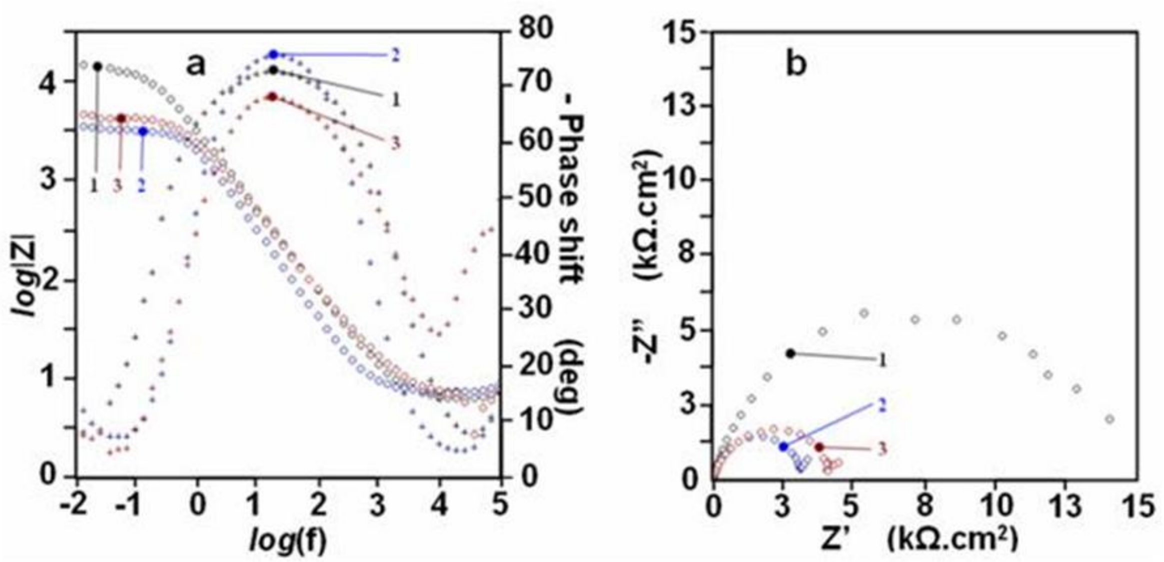

Fig. 1. Bode (a) and Nyquist (b) plots of the EI-spectra of three samples of Group 6. 1 – sample P1; 2 – sample P2; 3 – sample P3

concentrations of (NH4)2Ce(NO3)5, or after different preliminary treatments.

It is obvious that the first sample P1 remarkably excels the other two. The real part Z' of its Nyquist plot reaches 15 kΩ.cm^2 (curve 1), while the rest two stay between 3 and 5 kΩ.cm^2 (curves 2 and 3). The first one (P1) is prepared by higher content of cerous ammonium nitrate, as the second one (P2), but its substrate was prepared by only mechanical grinding in contrast to specimens P2 and P3.

This fact means that the alkaline preliminary treatment procedure possesses generally detrimental character. Although this approach is widely used for pretreatment of Al-alloys, it obviously modifies the metallic surface composition. In alkaline media, the Cu-containing Al alloys suffer preferential dissolution of the Al matrix surrounding the Cu-intermetallics. That is the reason for undermining and removal of the Cu-containing particles and the resulting superficial copper depletion. Furthermore, its impact is much more remarkable than the concentration of the basic substance in the coating solution. This fact is also obvious, because the difference between the samples prepared by 0.1 or 0.05 M of $(NH_4)_2Ce(NO_3)_5$ (curves 2 and 3) is negligible, compared to the difference of the preliminary treatment approaches (curves 1 and 2).

Regardless the weak difference between the samples coated by 0.05 and 0.1 M Ce-salt solutions, the one with lower Ce-content seems to possess better barrier properties (curves 2 and 3 in Fig. 1). Obviously, the presence of buffer compensates the double Ce-addition, by hindering of its deposition. Probably, it does not allow the local pH increment necessary for CeCC deposition, by formation of $Ce(OH)_3$/$Ce(OH)_4$ species. Besides, in the case of double addition of the Ce-compound (sample P2), the relation of the addition of H_2O_2 to the basic Ce-substance decreases. In other words, the coating solution for P2 contained 25 ml/l of H_2O_2 for 0.1 M $(NH_4)_2Ce(NO_3)_5$, and this relation was twice higher

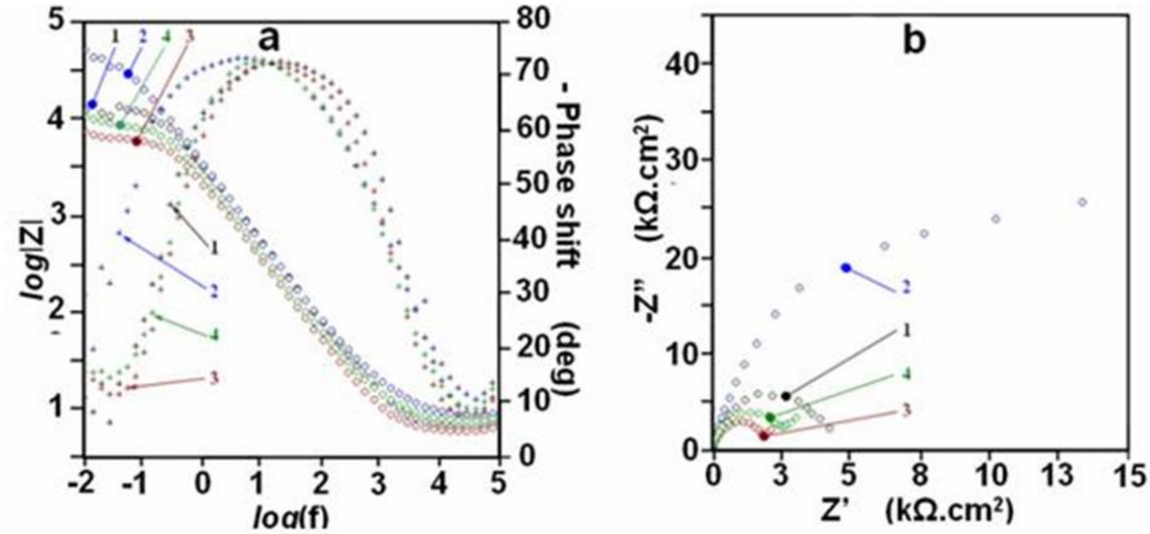

Fig. 2. Bode (a) and Nyquist (b) plots of the EI-spectra of CeCC coatings deposited after mechanical pretreatment and different H_2O_2 additions: 1 – sample P1, after 48 hours of exposition; 2 – sample P5 after 48 hours of exposition; 3 – sample P1 after 168 hours of exposition; 4 - sample P5 after 168 hours of exposition

for sample P3 (prepared with 25 ml/l. H_2O_2 but only 0.05 M. Ce-salt). That was the reason to compare the barrier ability and durability of two samples with equal addition of 0.1 M Ce-salt, and different additions of H_2O_2. The additions of the peroxide were 25 and 50 ml/l, for P1 and P5, respectively.

Experiments on samples with only 0.01 M content were performed, as well. All of the samples revealed completely unsatisfying results, regardless the preliminary treatment approach, oxidant additions, duration and temperature of coating deposition, applied on the respective substrate. This fact was the reason to terminate any further measurements on samples coated by this concentration of the Ce-compound.

Figure 2 contains impedance spectra, recorded for both mechanically pre-treated samples P1 and P5, after 48 and 168 hours of exposition to 3.5% NaCl model corrosive medium.

The spectra after 24 h of exposure had not clear shapes because the data points were strongly dissipated. This fact imposed evaluation of the sample barrier abilities by the spectra acquired after 48 hours (curves 1, and 2). The log|Z| = *f*(log(f) curve of the Bode plot for the sample with 50 ml / l of H_2O_2, at 0.01 Hz is by almost entire order of magnitude higher than this of the sample with only 25 ml/l of the oxidizer. The respective Nyquist plots reveal even higher difference. The analysis via "find circle" function, reveals that the total resistance $R_{total} = R_p + R_{coat}$ possess 15 kΩ.cm^2, compared to 50 kΩ.cm^2. On the basis of all these observations, it could be concluded, that the optimal ratio between the oxidizer and the basic ingredient is about 500 ml. of 30% H_2O_2, for each mol of $(NH_4)_2Ce(NO_3)_5$. This optimal ratio is correct only for the investigated system (i.e: between 0.05 and 0.1 mol of the Ce-salt, or P3, and P5, respectively). This ratio allows obtaining the highest barrier ability for the investigated system.

Nevertheless, it could be also concluded, comparing the curves 3 and 4 that they almost overlap. These curves were recorded after 168 hours of exposition of samples P1, and P5 to the corrosive medium. Regardless the fact that the P5 slightly excels P1, after one week of exposition the former one has obviously lost its barrier ability, (curves 2 and 4). The clear difference between the spectra recorded after 48 and 168 hours of exposition to the corrosive medium for the sample P5, reveal its low durability in these conditions.

Influence of pH of the coating solution was also followed. The pH value was maintained to be 2.00 by correction via dropping of HCl : H_2O (1 : 3). However, the sample P3 (prepared by mechanical and alkaline treatment of the substrate, and coating by 25 ml/l. H_2O_2 and 0.05 M. Ce-salt, with corrected pH = 2.00) was repeated by another sample P4, but with its own pH = 2.61.

The comparison between the spectra of samples P3 and P4 reveals that the specimen, coated by the bath with pH = 2.61 has much better barrier ability, than this one, with the pH = 2.00 corrected by acid addition. The log|Z| value at 0.01 Hz, for P4 excels by 1.5 orders of magnitude this one of P3. Additional difference between the respective Bode plots is that the curve φ = f(log(f)) possesses two, clearly distinguishable maxima. This fact undoubtedly evinces the presence of two superficial layers. It could be supposed that during the deposition of the Ce-conversion coating, additional oxide layer grows, due to the acidic nature of the coating solution. These conditions cause supplemental growth of Al-oxide layer on the sample P3, as well. However, because of absence of uniform film of CeCC, in the case of P3, its φ = *f*(log(f)) curve has only one maximum at the middle frequencies. It is originated from the Al-oxide layer appeared in the conditions, described above.

After 168 hours of exposition, the spectra remain their shapes. This fact is indication for the relatively good durability of both coatings. The Nyquist plots of P4 show that the real part (i.e: Z') of the semi-circles decrease from relatively 55 kΩ.cm^2, detected at 48 hours of exposition to 20 kΩ.cm^2 , after one week of exposure (Compare Fig. 3 (a, b) and (c, d)).

Linear polarization curves

When the cathodic curves acquired after 24 h. are compared, it becomes obvious that the buffer stabilizes the deposition process. The specimens P3, and P4, prepared without buffer reveal deviation from the rest. However, the lowest cathodic current density belongs to P4, whereas the highest one relays to P3. As a result, current density of the coating deposited at pH = 2.61, without buffer is about entire order of magnitude lower than the buffer assisted coatings. Reciprocally, the other coating deposited without buffer at pH = 2.00 possesses the highest current density.

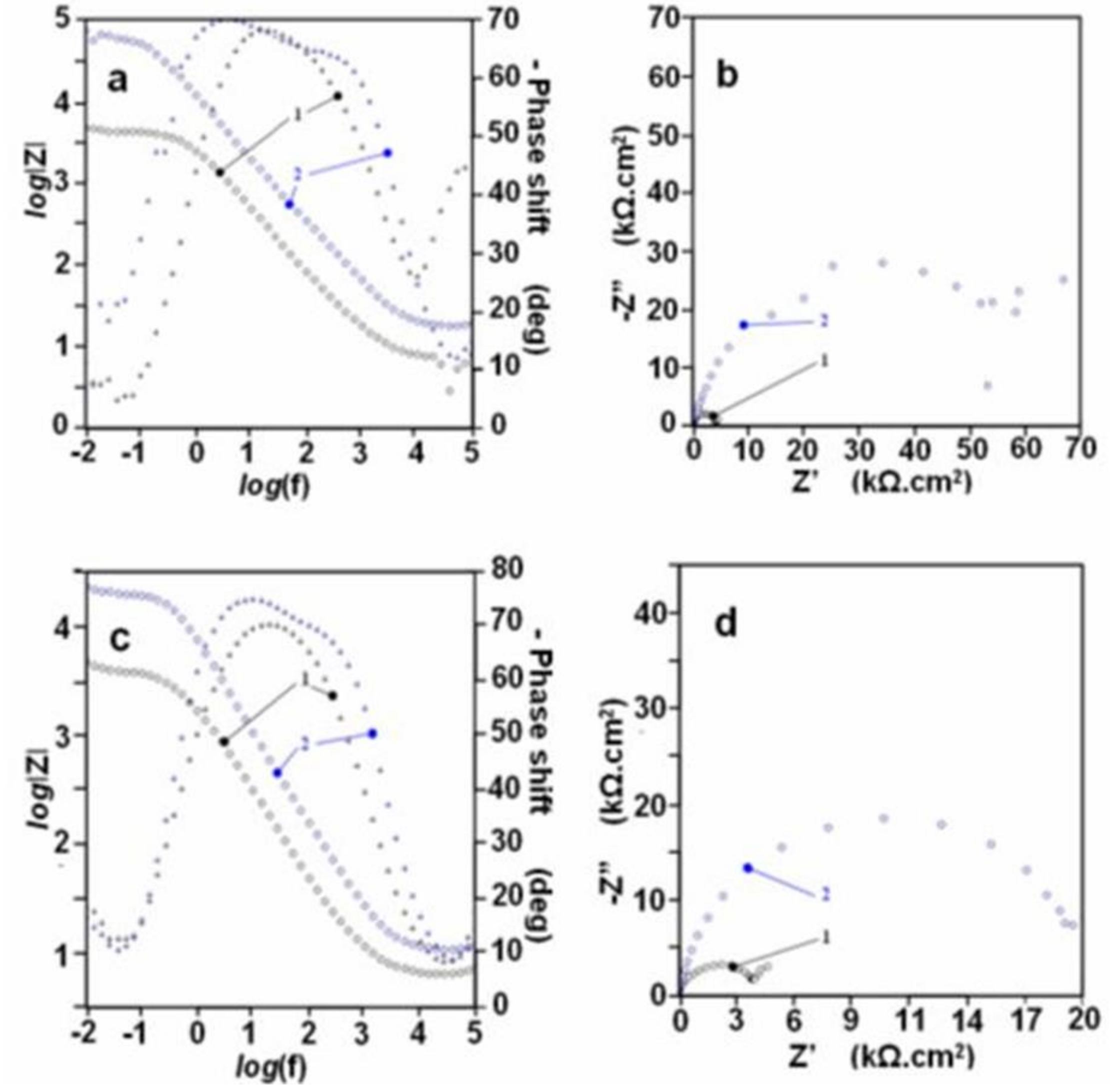

Fig. 3. Electrochemical Impedance Spectra recorded after 48 (a) and 168 (b) hours of exposure of two samples with different pH of the coating solutions. 1 – specimen P3; 2 – specimen P4.

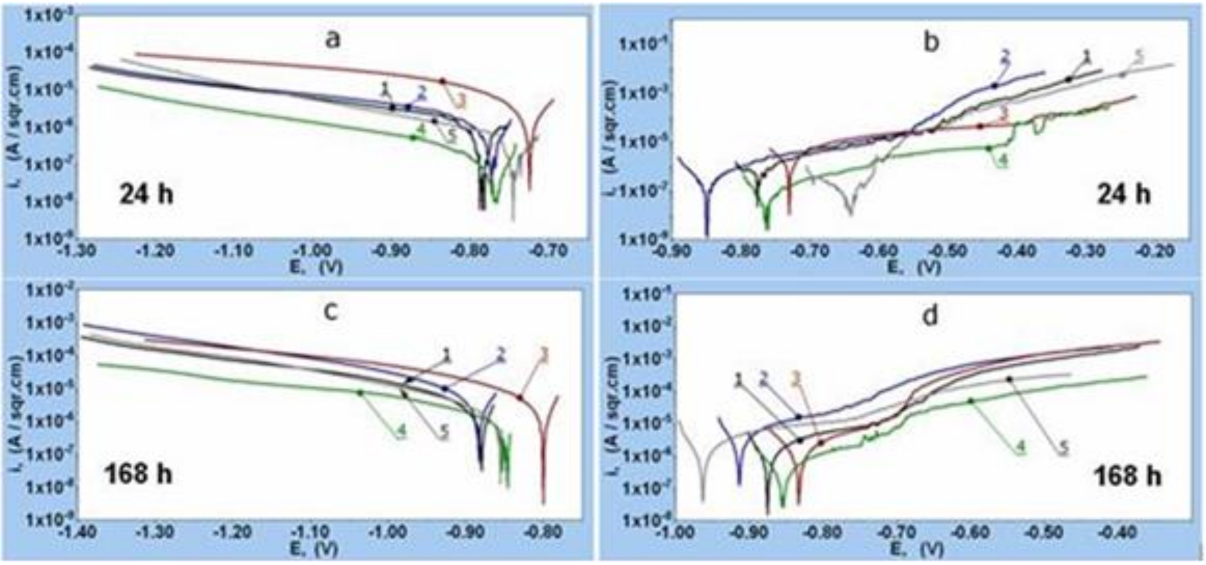

Fig. 4. LSV-curves of the samples acquired after 24 (a) and 168 (b) hours of exposition to 3.5% NaCl model corrosive medium. 1 – sample PI; 2 – sample P2, 3 – sample P3, 4 – sample P4, 1 – sample P5,

The respective anodic curves confirm the statements done for the cathodic ones. The lowest current density belongs to P4. In addition, the largest passivity region (between -760 and -410 mV) is attributed to this sample. The length of this region is described in [27] as a measure for “strength against pitting nucleation”. This measure, together with the lower corrosion current densities in both the cathodic and anodic polarization curves indicate that the barrier ability of sample P4 excels these of all the rest specimens in this study. Obviously, the relatively higher pH value (pH = 2.61) prevents severe attack to the oxide layer on the matrix, observed at pH = 2.00.

After 168 hours, the current densities of the respective cathodic and anodic curves for P4 still remain with up to about an order of magnitude lower than the rest, although the remarkable shortening of the passivity region of its anodic curve. Both these facts indicate that after 168 hours of exposition, the specimen prepared at higher pH is relatively more durable than the rest samples, regardless the loss of its strength against pitting nucleation.

Morphological characterization of the samples

The different behavior of the samples in corrosive medium reflect their individual structures, as consequence of the conditions applied for the deposition of the respective coatings. On the other hand, the structures of these coatings could be assessed by their superficial morphologies. For these reasons, SEM – observations were executed for description of the topographies of the coating surfaces. The respective SEM – images are shown in Fig. 5.

The SEM images reveal that the samples possess completely different morphologies. Even the preliminary treatments of the substrates result in the mechanism of coating deposition (compare positions (a) and (b)). The former has equally distributed morphology, while the latter reveals additional layer of deposits. The ratio between the Ce-salt, and the oxidant renders its influence, as well. The additional deposits observable for the sample P2 are presented neither for sample P3, nor for P4 (see positions (c) and (d)). This fact means that because of the lower content of oxidant, compared to the Ce-salt in the case of sample P2, there is not enough intensive precipitation of Ce-oxides/hydroxides.

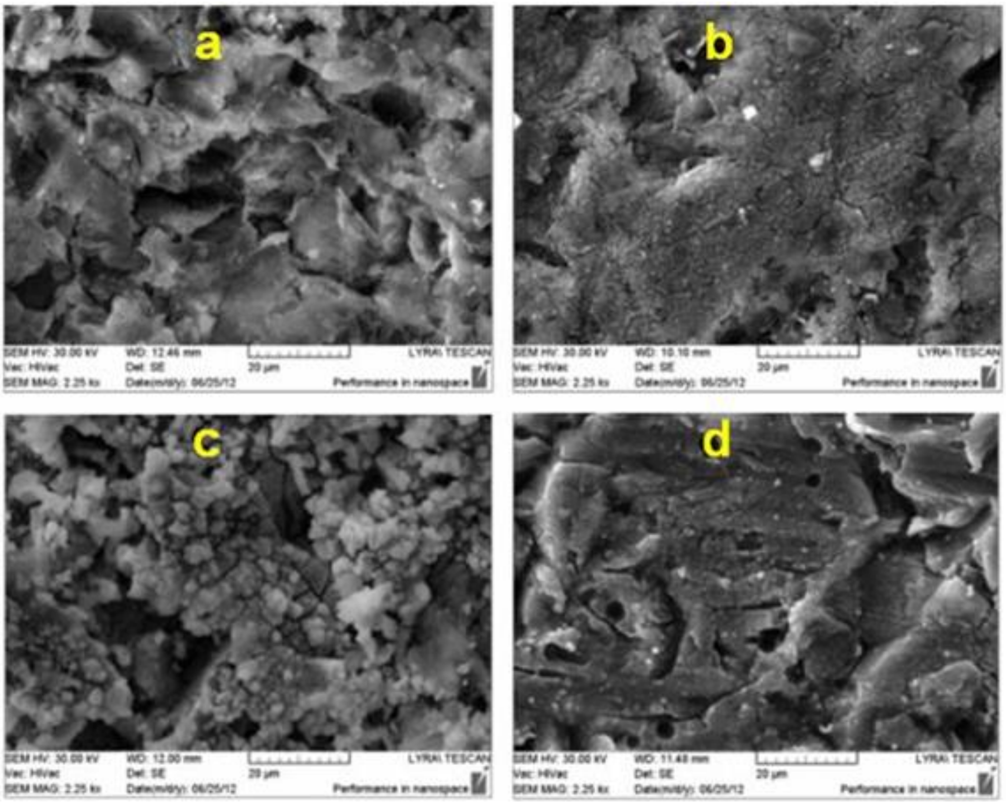

Fig. 5. SEM topological images of the investigated samples: a - specimen P1; b – specimen P2; c – specimen P3; d – specimen P4

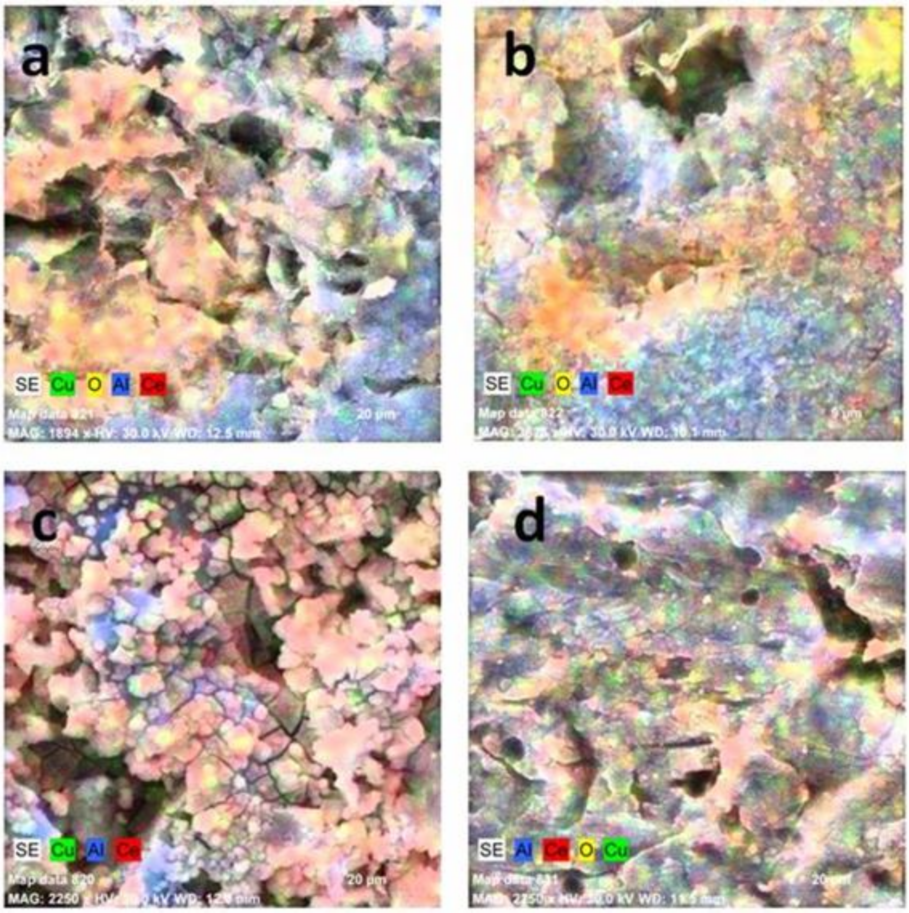

Fig. 6. EDS topological images of the investigated samples: a – specimen P1; b – specimen P2; c – specimen P3; d – specimen P4

As consequence, the coating deposition passes accompanied by corrosion process. That is the reason for the coverage of the Ce-coating by corrosion products, such as $Al(OH)_3$. The comparison between samples P3 and P4 (positions (c) and (d)) shows that the pH has strong influence during the deposition process. The unique difference between the samples is that the former coating was deposited at pH = 2.00, while the latter is done at pH = 2.61. The corresponding coatings possess entirely different morphology.

The EDS map analysis confirms the conclusions done for the SEM observations. The superficial sediments that cover the coating of P2 (see position (b), Fig. 6) are almost entirely composed by Al - compounds.

CONCLUSION

New electrolyte was elaborated, for deposition of Cerium based conversion coatings (CeCC) for protection of D16-AM alloy against corrosion. The cerium salt - Diammonium pentanitrocerate was used, in which, contrary to all rest electrolytes used up to nowadays, the Cerium is represented in the anionic moiety.

During its development, the influence of various conditions was elucidated, related to the preliminary treatment, the composition of the electrolyte, and the deposition regime.

It is demonstrated that the preliminary treatment has remarkable importance for the features of the coatings. Two basic approaches were employed for preliminary treatment of the D16-AM substrates: only mechanical grinding, or in combination with alkaline etching, and acidic activation. It is established that the coatings deposited after only mechanical treatment results in uniform films.

It is ascertained that the best Cerium Conversion Coatings are obtained by the following electrolyte composition: concentration of the Ce-salt 0.05 up to 0.1 M; molar ratio between the peroxide and the Ce-salt, from 4 to 8; pH about 2.6; and NaCl content – 35g/l.

It was observed that during the CeCC deposition, pH of the coating solution rises, resulting in undesirable precipitation of Ce-oxides/hydroxides. The maintenance of the electrolyte pH, in narrow optimal interval and to avoid the precipitation of the Ce-salt, the conversion bath was buffered by buffer of Lourier, based on amino-acid. Nevertheless, the addition of buffer should be compensated by higher Ce-content.

By SEM-EDS observations was evinced that even insignificant change of whatever parameter of the deposition process results in completely different superficial morphology of the coating.

By application of two, electrochemical methods independent between themselves: Linear Voltammetry and Electrochemical Impedance Spectroscopy, the barrier ability and the durability were investigated. As a result, it was established that the best specimen possesses the highest value for the total resistance $R_{total} = 5x10^4\ \Omega.cm^2$ which is a measure for the barrier properties of the coating.

After 168 hours of exposition, the CeCC deposited at higher pH on mechanically grinded substrate is relatively more durable than the rest samples, regardless the loss of its strength against pitting nucleation.

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ВЛИЯНИЕ НА УСЛОВИЯТА НА ОТЛАГАНЕ НА ПОКРИТИЯ ОТ Ce-КОНВЕРСИОННИ БАНИ ВЪРХУ СВОЙСТВАТА НА ПЛАКИРАНА СПЛАВ Д16 АМ

Д. С. Родригез[1], С. Кожухаров[2]*, М. Мачкова[2], В. Кожухаров[2]

[1]Университет Виго, Лагоас, Марконсенде 36310 (Испания)

[2]Химикотехнологичен и Металургичен Университет, бул. "Климент Охридски", София П.К 1756 (България)

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(Резюме)

Целта на Настоящата работа е да се оцени влиянието на различни условия върху спонтанното отлагане на цериеви конверсионни слоеве из разтвори на диамониев пентанитроцерат $(NH_4)_2Ce(NO_3)_5$ върху плакирана сплав Д16 АМ, покрита чрез потапяне в цериеви конверсионни вани, и да се проведе последващ анализ върху поведението и характеристиките на получените покрития. Техните охарактеризирания са проведени чрез тестове за устойчивост спрямо моделна корозионна среда, съставена от 3,5% разтвор на NaCl, съчетани с периодични електрохимични измервания и последващи морфологични охарактеризирания. Първият вид измервания бяха проведени чрез Електрохимична Импедансна Спектроскопия (ЕИС), съчетана с линейна волтамперометрия с линейна разгъвка на потенциала (ЛВА), а вторите бяха проведени чрез Сканираща Електронна Микроскопия (СЕМ), съчетана с Енергийно Разпределителен Рентгенов Анализ (ЕРРА). Като резултат, бяха определени оптималните условия за отлагане на цериеви конверсионни слоеве.