Influence of the interactions between the corrosion inhibitor and nano-containers over the corrosion protective capability of hybrid nano-composite pre-treatments

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Abstract: *The aim of the present research is to study corrosion protective ability of hybrid nano-composite pre-treatments, prepared with and without nano-particles, deposited on AA2024-T3 alloy. The interaction between Al_2O_3 nano-particles and inhibitor $CeCl_3$ was investigated. The measurements were performed via Electrochemical Impedance Spectroscopy (EIS) in 3%NaCl solution used as a model corrosive medium. The electrochemical results obtained illustrated a positive effect of nano-containers used for controlled release of inhibitor. It was established decrease of inhibitor losses due to its leaching effect and increasing the efficiency of the corrosion inhibition effect.*

Key words: *corrosion protection, $CeCl_3$ inhibitor, nanocomposite coatings, hybrid pre-treatments,EIS.*

INTRODUCTION

The aluminium and its alloys have significant importance due to their remarkable mechanical strength. Simultaneously, these alloys possess relatively low weight in comparison to the steels for example. As consequence of this specific combination of properties, these alloys are appropriate for various applications in the scope of the transport and especially for the aircraft industry. However, the exposure to an ambient environment, leads to corrosion of the metals and their alloys through charge transfer reactions, which may cause superficial deterioration of alloys. Worldwide, the metallic corrosion causes considerable waste of natural resources [1].

The highest attention was justly paid to the localized corrosion of AA2024 aluminum alloy, which is extensively used in the aerospace industry due to its excellent weight-to-strength ratio. The intermetallic particles segregated in the grain boundaries promoting enhanced mechanical properties, but at the same time they increase the susceptibility of the alloy to a localized corrosion attack [2].

In the industrial practice, the metallic substrates are pre-treated before their applications. Usually, primer pre-treatment is applied in order to improve adhesion between the metals surface and the upper paint layers [3].

Chromate conversion coatings have been widely applied for corrosion protection of aluminum alloys due to their self-healing nature, ease of application, high electrical conductivity and high efficiency/cost ratio. Moreover, they provide the greatest level of under film corrosion resistance and facilitate the application of further finishing treatment [1]. However, the use of chromium for the corrosion protection in the automotive industry has been banned since 2007 due to the “End of Live Vehicles” (ELV) directive, and in the electrical and electronics industry since 2006 by the “Restriction of Hazardous Substances” (RoHS) directive [4]. These actual directives have stimulated worldwide research activity over invention of new efficient and also environmentally-friendly substitutions of chromium compounds and other hard metals [5-7].

Nowadays the sol-gel approach for preparing of oxide protective films (coatings) has emerged as a versatile method [3]. All technologies which include sol or gel as intermediate stage could be concerned as “sol-gel technologies” [8, 9]. There is an actual review paper with focus on history of the sol-gel technology development [10].

Hybrid materials could be obtained via crosslinking of Me-O-Me chains by organic substances [10,11]. Haas and Rose [12] presented a conceptual review description of the hybrid materials, including their general classification. In addition, they have described the contribution of both of organic and inorganic parts of the hybrid materials, and its influence over the properties of the obtained materials. The advantages of the usage of these materials for corrosion protective pre-treatments and coatings are particularly remarked by Mackenzie [13]. Furthermore, in order to improve the performance of these materials, corrosion inhibitors in pre-treatments are added by nano-particles. The purpouse of this approach is to avoid the leaching of the inhibitor from the zones of corrosion. It is achievable by the use of the nano-particles as containers of inhibitor, which provide its controlled release, as it is well described by [5].

The aim of present experimental research is to establish whether there is synergetic effect between the inhibitor and the nanocontainers, as it is described in the literature for similar systems. That effect should be expressed in the controlled releasing of the inhibitor ($CeCl_3$) from the paint system (pre-treatment). In order to determine whether the nano-particles provide controlled release of the inhibitor, comparative measurements between bare metal and two pre-treated samples were done. The pre-treatments were with and without of nano-particles, respectively. Electrochemical Impedance Spectroscopy (EIS) method was applied for tests execution.

EXPERIMENTAL PROCEDURE

Samples preparation

Samples object of the present research are summarized in Table 1:

Table 1 Compositions of the samples

Sample Index	Substrate	Pre-treatment	Nanoparticles	Inhibitor
S1	AA2024-T3	--------	--------------	--------------
S2	AA2024-T3	GMT	--------------	4%$CeCl_3$
S3	AA2024-T3	GMT	30% Al_2O_3	4%$CeCl_3$

Detailed description of GMT-hybrid matrix could be found in ref. [3,14] and it was object of a patent [15] as well. The procedures of preparation of the nano-particles, as well as their characteristics are described in detail by Schem et al. [4]. Briefly, should be mentioned that the nanoparticles are represented by powder material, including nano-agglomerates with size 500nm, of nano-particles with size 10-15nm, and specific surface - 111m^2 /g, respectively.

Equipment and cell

Potentiostat-Galvanostat PGSTAT 30/2, produced by Ecochemie-Netherlands was used for EIS measurements. Three-electrode's cell with volume, equal to 100ml was used (Fig. 1-a). All of the tests were performed at room temperature in 3% NaCl solution. A part of the surface of samples-object of measurements, with form of circle and area 0.64cm^2 served as “working electrode” (WE). The counter electrode (CE see Fig. 1-a) was performed by platinum net with highly developed area. The referent electrode (RE) was a standard Ag/AgCl electrode, model G. 0726.100 of Metrohn. All of the impedance spectra were measured at Open Circuit Potential (OCP), signal amplitude of 100 mV and frequency range from 10^5 to 10^{-2} Hz at 7 frequencies per decade.

Test procedures

In order to evaluate the influence of the approach of usage of nano-containers for controlled release of inhibitor over the corrosion protective capabilities, the following procedures were performed. First, the samples were prepared either by direct addition of inhibitor, or by inhibitor loaded-nanoparticles, as they are described in Table 1. Afterwards artificial defects-pinholes were made on their surface. The deepness was enough to achieve the metal surface. After that, the samples have been exposed to the corrosive medium for one month (720 hours). The reference sample (index S1) has been exposed for 24 hours. It was not necessary to expose this sample for larger periods, because it should release much more corrosion products which could contaminate the medium (the electrolyte). The contaminations should lead to significant changes of the further corrosion processes, by pH changes for example. The EIS measurements were performed in a current way once per week.

RESULTS AND DISCUSSIONS

It should be noted that the quality of the pre-treatments depends on its characteristics. Pre-treatment characteristics predetermine their performance in the corrosive medium. They should act as mechanical barrier between the substrate and the aggressive environment. In this context, they perform a passive corrosion protection. Consequently, they should possess mechanical strength, and adhesion of the pre-treatments is related to the passive corrosion protection. In addition, they must protect the metal surface even after defect initiation in their structure by release of corrosion inhibitors. This phenomenon is known as "self healing effect" [16] and it corresponds to an active corrosion protection behaviour.

Figure 1 shows impedance spectra of samples S2 and S3 after different exposure times. For comparison, the spectrum after 24h of bare alloy is also given.

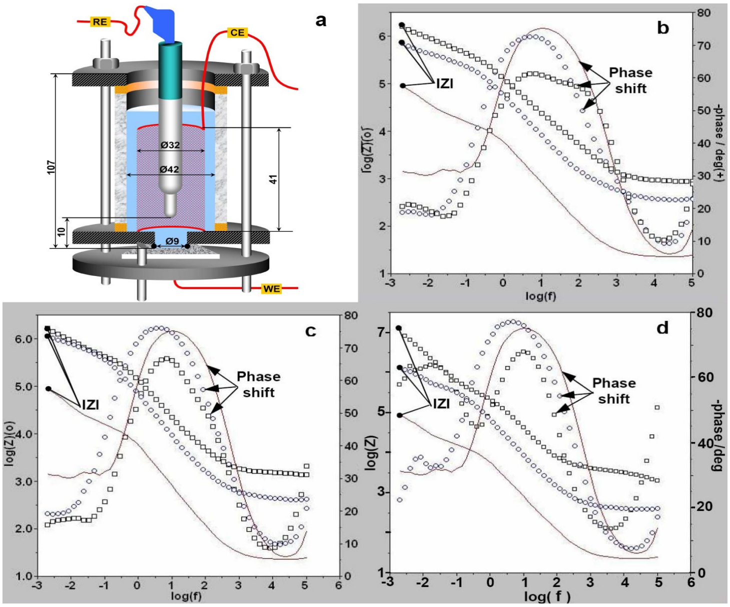

Figure 1 (a)-Schematic view of the three-electrode cell used; (b)- Bode plots of EIS spectra after 168 h; (c)- 236 h and (d)- 720 h – exposure time; Samples: S1- after 24 h of exposure, marked by continuous line, S2 – circles and S3 –squares.

Figure 1 illustrates a well expressed difference between the characteristics of samples S2 and S3. The phase shift of the S2 - spectrum is much more close to the S1-spectrum. Both coating samples not containing Al_2O_3 nano- particles. In addition, at the middle frequency region of the spectra, the sample with inhibitor, involved into nano-particles (S3) reveal two different maxima (Fig.1-b). The latter disappears after one month exposure time (see Fig. 1-d). It should be noted that any presence of second maximum is not observable for the case of the sample prepared by direct addition of inhibitor to GMT-matrix. This fact undoubtedly means that the inhibitor is already expensed even before the first 168 hours of exposure. In addition, at low frequency region of all spectra (Fig. 1- b, c, and d), another difference could be checked. The module of the impedance for the sample prepared by inhibitor loaded nano-particles (S3) is with relatively one order of magnitude higher, than this one which is prepared by direct involvement (S2). These differences between the spectra of both of samples are clear expression of the prolonged activity of the inhibitor in the case of presence of nano-particles. Consequently, the nano-particles hinder the release of the inhibitor, and retain its leaching from the zone of the corrosion activity i.e. they improve the performance of the inhibitor used.

It is necessary to mark that the mechanism of the Ce- salts inhibiting effect is described in the literature [6], and it is based on the precipitation of $Ce(OH)_3$ and $Ce(OH)_4$. The corresponding hydroxides are products of chemical reactions between the Ce-ions from the dissolved $CeCl_3$ and the OH^- from the electrolyte. It could be accepted that the deposits of these insoluble hydroxides over the substrate's surface limit the area of directly exposed zone of the substrate to the electrolyte.

Figure 2 shows a model for leaching of the inhibitor according to the concept of Zheludkevich et.al. [6].

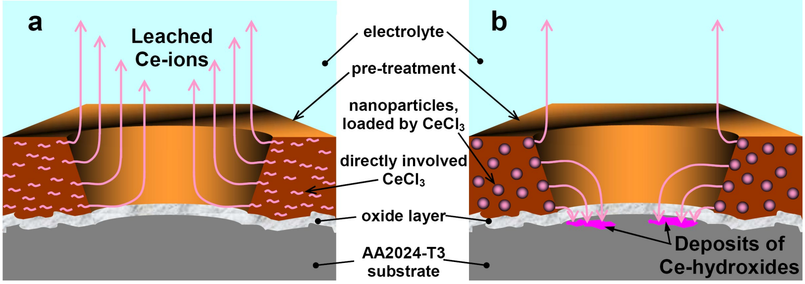

Figure 2. 3D schematic view for the roll of nano-containers for decrease of the undesirable leaching of the inhibitor; (a) – inhibitor involved directly to GMT-matrix and (b) – inhibitor loaded nano-particles.

The roll of the nano-particles as inhibitor containers is to provide controlled gradual release of the inhibitor. Namely they hinder the inhibitor's leaching. This process of leaching is strongly undesirable phenomenon because it leads to loss of the inhibitor. Due to the leaching effect, the inhibitor goes to the bulk of the electrolyte instead of to the corrosion zone. This is the reason to use the approach of loading of nano-particles by the inhibitor before its involvement into the gel-matrix.

CONCLUSIONS

The following general conclusions could be extracted:

1. The differences of the spectra of S2 and S3 are clear evidence for the positive effect of usage of nano-containers for controlled release of the inhibitor used.

2. The nano-containers decrease the losses of inhibitor due to its leaching, and undoubtedly increasing the efficiency of the corrosion inhibition effect.

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Докладът е рецензиран.