Influence of the processes of additional phosphate post-treatment of ceria conversion coatings deposited on Al 1050 on their corrosion protective behavior

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Abstract. Systematic studies were carried out with respect to the elucidation of the role of additional “post-treatment” immersion phosphate processing on conversion corrosion protective ceria coatings CCOC deposited on aluminium Al 1050. Thereupon, the influence of various compositions of the CCOC as well as the conditions of such treatment were studied, based on solutions of Na₃PO₄ or NH₄H₂PO₄. The results obtained with respect to the corrosion behavior, respectively the corresponding changes in the chemical composition of the studied corrosion-protective systems, give us the reason to suppose that the phosphate layers formed on the CCOC play the role of not only protective barrier coating, but they also change the kinetics of the conjugated electrochemical reactions characterizing the corrosion of aluminium. Key words: aluminum, pre-treatment, cerium-containing conversion films, corrosion

1. Introduction

As a result of the investigations carried out intensively during the last years to replace the highly effective chromate protective films on aluminum used until recently [1], it was ascertained that among the most successful alternatives are those connected with the application of conversion oxide coatings prepared from solutions containing ions of metals belonging to the lanthanide group [2]. The best results, from corrosion point of view, have been shown by the conversion cerium-oxide coatings (CCOC) [3,4]. They form on the surface of aluminum insoluble hydroxides/oxides, which are acceptable from ecological and health protection points of view, in addition to their efficient corrosion protection ability [5].

However, during the application of the compositions and conditions for conversion treatment of aluminum elaborated on the basis of cerium salts, the high degree of protection manifested by the chromate films has not yet been achieved. Encouraging results in this respect have been obtained in the case of involving an additional finishing sealing of the deposited CCOC in solutions of various phosphate compounds [2]. Such an approach leads both to the additional formation of insoluble aluminum phosphates, as well as to a synergistic protective effect between CCOC and the metal phosphate combined layer formed upon it, in which the metal could be Ce, Al or Al+Ce [6].

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Moreover, some authors suppose that the formation of phosphate layers (PHL) upon CCOC influences favorably their degree of fracturing, which leads to an enhancement of their protective ability [7].

In this connection, the aim of the present study was to find out what the influence is of the composition and the conditions of the additional (“post-treatment”) phosphate processing of the coated with CCOC support of Al 1050. Thereupon, an attempt was made to establish the effect of the amount of cerium in the deposited CCOC [8] and the chemical nature of the phosphate salt, respectively the phosphate ion, included in the solution for the formation of PHL.

2. Experimental

Coatings of CCOC were deposited on substrates of “technically pure” Al 1050 (containing 0.40% Fe, 0.25% Si, 0.05% Mn, 0.05% Cu, 0.07% Zn, 0.05% Mg), widely applied as a construction material. The studied samples of dimensions 1×2 cm were cut out of rolled Al sheets of thickness 0.1 cm. Their pre-treatment involved degreasing in organic solvent, degreasing (chemical cleaning) in aqueous solution of NaOH (Al/NaOH) or chemical cleaning in NaOH and consecutive etching and surface activation in HNO₃ (Al/(NaOH+HNO₃)) at room temperature, as described in [9].

We achieved the formation of CCOC by using a solution containing 0.5 M CeCl₃×7H₂O + 1×10⁻⁵ M CuCl₂×2H₂O. No H₂O₂ or other types of oxidizing agent were added. The investigations were carried out at pH = 4.1, temperature of deposition 25 °C and time interval of deposition 120 min.

The post-treatment of CCOC as-deposited on an Al substrate (Al (NaOH or NaOH+HNO₃)/Ce+Cu) aiming at an additional formation of phosphate layers on them was realized in two types of phosphate-containing [6] solutions: 0.08 M Na₃PO₄ (Al (NaOH or NaOH+HNO₃)/Ce+Cu/Na₃PO₄) and 0.22 M NH₄H₂PO₄ (Al (NaOH or NaOH+HNO₃)/Ce+Cu/NH₄H₂PO₄). The working solutions were carried out at pH = −4.4, temperature of deposition 85 °C and time of immersion 5 min.

The morphology (SEM), chemical composition (EDS), electrochemical characteristics and corrosion performance in model corrosion (0.1 M NaCl) media (characterized by E-lgi and E-t curves, degree of corrosion protection (z, %) of CCOC on Al 1050, containing different contents of Ce(VI)₃(Ce₂O₃) and Ce(III)₃(Ce₂O₃) were examined as a function of the phosphate post-treatment in solutions of Na₃PO₄ and NH₄H₂PO₄. More details about the experimental techniques can be seen in ref. [8].

3. Results and discussion

Figure 1a is a SEM micro-photograph of the surface of CCOC deposited on Al 1050 after its preliminary treatment (pre-treatment) in 1.5 M NaOH and its immersion treatment in a solution of 0.5 M CeCl₃×7H₂O + 1×10⁻⁵ M CuCl₂×2H₂O. Figure 1b illustrates the same surface after the deposited CCOC was subjected to consecutive immersion treatment (post-treatment) in a solution of Na₃PO₄ (figure 1b) or NH₄H₂PO₄ (figure 1c). Below the figures, the results of EDS analyses are also given for each one of the studied samples characterizing the chemical composition of the surface of CCOC, respectively its change caused by the post-treatment operations in the two types of phosphate solutions.

It follows from the presented results that after this preliminary treatment (in 1.5 M NaOH) of the aluminum substrate, the formed CCOC are built up of spherical agglomerates, which are relatively uniformly distributed over the entire surface, reproducing the profile of the Al substrates. Therefore, the roughness and the rigidity determined by the mechanical treatment of the rolled Al 1050 sheet influence in a specific way the formation of the chemically deposited copper clusters [10], on which CCOC is deposited predominantly [8]. One does not observe any cracks and defects in the layers. The EDS analyses detect only the presence of Ce (4.2%) and no Fe is found (component of Al substrate) and (chemically deposited) Cu. The results from these analyses point to the high density and uniform thickness of CCOC, whose formation is initiated by the active cathode sections (Cu and Fe) on the aluminum surface.

Figure 1b, characterizing the surface of the sample coated with CCOC and subjected to an additional post-treatment in Na₃PO₄, shows that the phosphate immersion layer is not distributed
uniformly over the entire surface. It has some island-like distribution (inset 2 in figure 1b), whereupon on the larger section of the surface of the sample the phosphate layer is not observed (inset 1 in figure 1b). The integral EDS analyses of the surface of this sample ascertained that the concentration of Ce (4.3%) is practically the same as that of the sample not subjected to additional phosphate treatment (figure 1a). In addition to these findings, P (2.4%) and Fe (0.7%) are also registered. The registering of iron and the unchanged concentration of cerium supply indications about the fact that in specific sections (mainly in the prevailing dark zones – inset 1 in figure 1b), the energy dispersion analysis detects the presence of Fe on the surface of the sample. Therefore, as a consequence of the phosphate post-treatment in Na₃PO₄, some sections of the Al substrate have become bare, containing Al₃Fe intermetallic compounds, which are characteristic of the aluminum matrix of Al 1050.

Figure 1. SEM surface image (at different magnifications and zones) and data of EDS analysis of as-deposited CCOC on pre-treated in 1.5 M NaOH Al 1050 substrate – a; as-deposited CCOC after its post-treatment in Na₃PO₄ – b; and as-deposited CCOC after its post-treatment in NH₄H₂PO₄ – c.

When the samples coated with CCOC were subjected to an additional post-treatment in NH₄H₂PO₄, the phosphate layer formed covered completely the entire surface of the sample (figure 1c). However, one can observe in it non-sealed sections similar to cracks, having a width of ~0.5-1.0 μm. The EDS analyses of these samples ascertained that the concentration of Ce (~2 %) is about twice lower in comparison with that of the non-treated CCOC (~4.2%). Cu and Fe are not registered, while the concentration of P (0.8%) is about four times lower in comparison with that found in the case of post-treatment in Na₃PO₄ (2.4%). The more than two-fold reduction in the registered concentration of Ce in this case shows that the phosphate film deposited by immersion, although thinner (P content 0.8% vs. 2.4% in the samples, having phosphate treatment in Na₃PO₄), is screening about twice as strongly the CCOC located below it. These results give us the reason to suppose also that defects similar to cracks in the phosphate film (figure 1c) most probably do not reach the sub-layer of CCOC located below.

Figure 2a is a SEM micrograph of the surface of CCOC deposited on Al 1050 after its pre-treatment in 1.5 M NaOH, followed by a treatment in 5 M HNO₃ and its immersion treatment in solution of 0.5 M CeCl₃×7H₂O + 1×10⁻⁸ M CuCl₂×2H₂O. Figure 2b and figure 2c present the same
surface, after the CCOC was subjected to a consecutive immersion treatment (post-treatment) in a solution of Na₃PO₄ (figure 2b) or NH₄H₂PO₄ (figure 2c). The results of the EDS analyses are also listed below the figures for each one of the samples studied.

It follows from the presented results that after this preliminary treatment (in 1.5 M NaOH and in 5 M HNO₃) of the aluminum substrate, the CCOC being formed are built up and dominated by spherical agglomerates, whose degree of sealing and the regularity of ordering is very high (figure 2a – the light zones). In our opinion, this result is determined by the additional preliminary treatment of the Al substrate in 5 M HNO₃, leading to the strong de-oxidation of its surface after the treatment in 1.5 M NaOH. Thereupon, the thick oxide layers, being formed on the surface, are practically completely removed [8].

![Figure 2](image.png)

**Figure 2.** SEM surface image (at different magnifications and zones) and data of EDS analysis of as-deposited CCOC on consecutively pre-treated in 1.5 M NaOH and 5 M HNO₃ Al 1050 substrate – a; as-deposited CCOC after its post-treatment in Na₃PO₄ – b; and as-deposited CCOC after its post-treatment in NH₄H₂PO₄ – c.

At the same time, it leads also to the appearance to a maximal extent of inter-metallic compounds of the type Al₃Fe, which are characteristic of Al 1050 [11]. These two effects accelerate substantially the kinetics of formation of copper clusters on the Al substrate – both on the cathode Al₃Fe sections, as well as on the other active sites (structural defects) on the aluminum surface. These, in their turn, facilitate the chemical deposition of defect-free conversion cerium oxide coatings having a high degree of uniformity of their thickness on Al 1050. In this connection, the integral EDS analysis detects only the presence of Ce and no presence of Fe and Cu is observed. The spot analyses in the light zones (figure 2a, item 1) confirm concentration of Ce above 12%, while in the dark sections around them (figure 2a, item 2) the concentration of Ce is ~ 3%.

Figure 2b, characterizing the surface of the sample coated with CCOC subjected to an additional post-treatment in Na₃PO₄, is differing substantially compared to the sample shown in figure 1b. Its morphology and structure are similar to those of the sample coated with CCOC, shown in figure 2a. The EDS analyses, in this case, established higher (with respect to the preliminary treated samples only in 1.5 M NaOH and phosphate treated in Na₃PO₄ samples – figure 1b) concentrations of Ce (8%)
and P (2.9%). Moreover, Fe (0.6%) and Cu (0.7%) are registered. The presence of iron and copper on the surface of the conversion film gives us reasons to draw the conclusion that in the latter case (as a consequence of the treatment in Na3PO4) some sections are detached, in which the conversion film is either very thin or is missing.

When the samples coated with CCOC are subjected to an additional post-treatment in NH4H2PO4, the phosphate film so formed covers completely the entire surface of the sample (figure 2c). It is similar in its structure and morphology to the sample presented in figure 1c. In it, however, one cannot observe the defects resembling cracks in the phosphate film, registered in figure 1c. The EDS analysis of this sample estimated the concentration of Ce as being (~1.2%), which is about four times lower in comparison with that of the non-treated in NH4H2PO4 CCOC (~ 4.8%). One registers additionally Fe (0.4%) and P (0.8%), whose concentration is about four times lower in comparison with that established in the case of post-treatment in Na3PO4 (P 2.9% - figure 2b). The almost four fold lowering of the registered concentration of Ce (Ce content 1.2% vs. 4.8% for the non-phosphate treated CCOC), as well as the presence of Fe and P on the surface of the protective system formed by conversion, indicates the fact that it is thinner and screens the aluminum substrate to a lesser extent.

Figures 3 and 4 present the polarization curves in coordinates E-lgi obtained in 0.1 M NaCl for samples having formed CCOC after preliminary activation of the aluminum substrate in a solution of NaOH (figure 3) and two-stage preliminary treatment in solutions of NaOH and HNO3 (figure 4), sealed respectively in solutions of Na3PO4 and NH4H2PO4.

**Figure 3.** Polarization curves of systems tested in 0.1 M NaCl at 25 °C.

**Figure 4.** Polarization curves of systems tested in 0.1 M NaCl at 25 °C.

One can see in figure 3 that after the preliminary activation of the aluminum substrate in a solution of NaOH, the sealing of the samples in a solution of NH4H2PO4 determines the strongly expressed influence on the kinetics of the cathode reaction of reduction of oxygen in the model corrosive medium, which is reflected on the enhancement of the corrosion protection degree (Table 1). When the preliminary activation of the aluminum substrate is carried out in a solution of NaOH and consecutive de-oxidation in HNO3 (figure 4), the post-treatment in both types of phosphate solutions leads to a substantial shift of the anodic potential dynamic curves towards more positive potentials and lower values of the corrosion currents under the conditions of anodic polarization (Table 1). In this case, the treatment in a solution of NH4H2PO4 exerts a more strongly expressed barrier effect in regard to the processes of anodic dissolution of the aluminum substrate. A characteristic feature of the anodic potential dynamic curves is the absence of a zone of passive state, which justifies the consideration that the corrosion potential of the studied systems coincides with the potential of pitting formation. This coincidence is a prerequisite for the local character of the corrosion process under the conditions of stationary corrosion. This means that the definite protection degree Z (Table 1) obtained by treatment of the samples in a solution of NH4H2PO4 characterizes both the protection from total
corrosion and from local corrosion in the model corrosive medium. The results obtained show that the phosphate cerium oxide conversion films are not only static barrier coatings, but they also change the kinetics of the conjugated electrochemical reactions characterizing the corrosion process in 0.1 M NaCl, i.e. they also determine the electrochemical protection.

Table 1. Electrochemical parameters determined from potentiodynamic polarization E-i curves: $i_{\text{corr}}$ – corrosion current; $E_{\text{corr}}$ – corrosion potential; Z – degree of protection.

| Samples/regimes of pre- and posttreatment under investigations | $i_{\text{corr}}, \text{A.cm}^{-2}$ | $E_{\text{corr}}, \text{V}$ | Z, % |
|----------------------------------------------------------------|-----------------------------------|-----------------|------|
| 1 Al 1050                                                       | 8x10^{-6}                         | -0.660          |      |
| 2 Al (NaOH)/Ce+Cu                                               | 1x10^{-6}                         | -0.695          | 87.5 |
| 3 Al (NaOH)/Ce+Cu/Na$_3$PO$_4$                                  | 6.3x10^{-6}                      | -0.612          | 21.3 |
| 4 Al (NaOH)/Ce+Cu/NH$_4$H$_2$PO$_4$                             | 2.4x10^{-7}                      | -0.649          | 97.0 |
| 5 Al (NaOH+HNO$_3$)/Ce+Cu                                       | 4x10^{-7}                        | -0.700          | 95.0 |
| 6 Al (NaOH+HNO$_3$)/Ce+Cu/Na$_3$PO$_4$                          | 3.5x10^{-6}                      | -0.586          | 56.3 |
| 7 Al (NaOH+HNO$_3$)/Ce+Cu/NH$_4$H$_2$PO$_4$                     | 8.9x10^{-7}                      | -0.531          | 88.9 |

4. Conclusions

It was established that the preliminary treatment of Al 1050 in alkaline and acidic solutions influences substantially the morphology, the structure and the composition of the CCOC corrosion protective films being formed on it. This effect is explained by initiating the operation of the active cathode sections (Cu and Fe) on the aluminum surface, which leads to improvement and optimization of the regularity of the ordering, the density and the chemical composition of CCOC. It was also shown that the additional post-treatment of the as-deposited CCOC in solutions of Na$_3$PO$_4$ or NH$_4$H$_2$PO$_4$, determining the formation of immersion PHL, promotes substantially the protective efficiency of CCOC. The latter fact is connected both with the variation of the kinetics of conjugated electrochemical reactions, induced by them, characterizing the corrosion process (i.e. the achievement of the effect of electrochemical defense – in the case of formation of PHL in a solution of Na$_3$PO$_4$), as well as with the strongly expressed barrier effect in regard to the processes of anodic dissolution of the aluminum substrate (in the case of treatment in a solution of NH$_4$H$_2$PO$_4$).

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