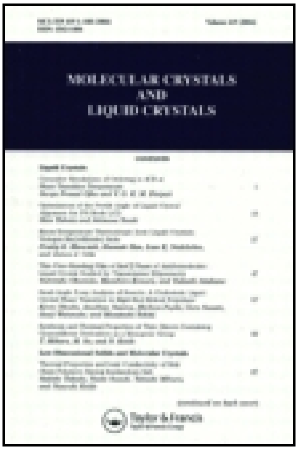

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Lithium-AluminIum Hydroxide Hydrate thin Layers on Al Based Substrates - New Ecological Process for Corrosion Resistance Increase

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LITHIUM-ALUMINIUM HYDROXIDE HYDRATE THIN LAYERS ON Al BASED SUBSTRATES - NEW ECOLOGICAL PROCESS FOR CORROSION RESISTANCE INCREASE

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Some preliminary experimental results on development of non-conventional, environmentally friendly procedures to form new corrosion protective thin films on Al, based on lithium-aluminium hydroxides known as hydrotalcite coatings, are presented. Chemical conversion films on pure Al and AU4G1 Al alloy have been formed involving $LiNO_3$*-*KNO_3*-LiOH based solutions, with/without a second step involving Ce (III) and Mn (VII) compounds. SEM pictures revealed a uniform layer, formed by crystallites with 200–300 nm walls length. Corrosion experiments showed their excellent performances, materialised in corrosion currents of 0.1–0.2* $\mu A/cm^2$ *and at least 168 hours of salt mist exposure with no aspect modification.*

Keywords: Al surface treatments; conversion coatings; hydrotalcite thin films

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INTRODUCTION

Aluminium is one of the most used materials in various fields of electrical engineering, electronics or aeronautics. Thus, depending on the applied surface treatments, various coatings types may be formed, as coating layers with decorative-anticorrosive properties, as adherent pre-treatment for organic finishing, as composite materials with special functional characteristics, thanks to their very well ordered structures, sometimes with nanometric sizes.

An important role in Al surface treatments has been assigned to Cr(VI) compounds, both in anodising and chemical conversion or sealing [1–3].

Because of their toxicity for environment and human health, many trials have been and are done to find viable alternative solutions to partially or totally replace them. Thus, various processes have been proposed, involving other transitional metal - containing anions, such as: molybdates, tungstates, and vanadates [4–9] with/without addition of lanthanide compounds [10–15].

A novel alternative for chromate conversion coatings is based upon the use of lithium-aluminium-anion-hydroxides (hydrotalcite type, HT), that showed good corrosion resistant properties [16–18], is easy to apply and relatively cheap.

In order to recommend hydrotalcite type coatings, additional information are needed to acquire and understand, regarding their processing, composition, morphology and anticorrosive properties offered to Al based substrates.

Usually hydrotalcite conversion coatings are formed by immersion in alkaline lithium salt solutions. Depending on the used anion, carbonates or nitrates are intercalated between Li-Al hydroxide layers allowing to form a complex structure that offers both corrosion protection, paint adhesion and coloured dye retention. Drewien *et al.* [18] analysed the composition and structure of the material, proposing a stoichiometry of approximately $Li_2Al_4CO_3(OH)_{12}\cdot 3H_2O$, based on TGA-FTIR, SIMS, Raman and XRD investigations, in the case of a lithium carbonate-lithium hydroxide conversion solution. Based on EIS investigations during 24 hours exposure to aerated 0.5 M NaCl, it was highlighted the good corrosion protection assured by hydrotalcite based coatings involving nitrate as oxoanion, especially when they are modified through Ce (III) or Mn (VII) species incorporation [16].

With this in view, the paper presents some preliminary experimental results regarding formation and corrosion behaviour of hydrotalcite type coatings-HTCCs on Al substrates, with or without Ce or Mn species insertions, as non-chromate, environmentally friendly finishing alternatives.

EXPERIMENTAL

To perform experiments, Al foils of min. 99.5% purity (annealed), Al sheets of industrial use (#1 mm), of min. 99.5% purity and Al alloy type AU4G1 (# 3.2 mm) provided by METAV SA Bucharest with the following chemical composition (%).

Cu	Mg	Si	Fe	Mn	Ni	Zn	Ti + Zr	Cr
3.80 – 4.90	1.20 – 1.80	Max.0.50	Max. 0.50	0.30 – 0.90	-	Max. 0.25	Max. 0.25	Max. 0.10

Before chemical conversion, the surface was subjected to a chemical degreasing in an alkaline solution [19,20] for 5 min., followed by a chemical deoxidising in HNO_3 1:1 (vol.), sometimes with a small addition of $CeCl_3$ for 30–60 s at room temperature. To form chemical conversion coatings, solutions containing: 6.9 g/L $LiNO_3$ – 28.3 g/L KNO_3 – 2.4 g/L LiOH have been involved, with $pH = 12 - 12.5$, at temperatures between 25 – 90°C, for various immersion periods, up to 30 minutes. Sometimes there has been applied a second sealing step either in 0.05M $Ce(NO_3)_3$ at room temperature for 20 minutes or in 2 g/L $KMnO_4$ at 70–80°C for 20 minutes. The samples have been rinsed with distilled water, dried and let at least 24 hours in air before starting electrochemical experiments.

To get information on chemical conversion processes, recording of open circuit potential as a function of time has performed, using a PM2422A Philips digital multimeter and a Zahner IM6e Electrochemical System, against a saturated calomel reference electrode, SCE. The coating mass and the amount of aluminium dissolved from the metallic specimen in order to further evaluate the coating ratio R has been estimated by gravimetric method [21,22], weighing the samples initially and after conversion process, as well as after coating removal in a phosphochromic solution (35 mL/L H_3PO_4-20 g/L CrO_3) at 100°C. To evaluate corrosion behaviour, potentiodynamic polarisation curves have been recorded in aerated 0.5 M NaCl, against a SCE reference electrode and Pt mesh counterelectrode, with a sweeping rate of 1 mV/s, using Zahner IM6e Electrochemical System. The geometrical surface of working electrode was 1 cm^2. Accelerated laboratory tests involved continuous immersion in 0.5 M NaCl at room temperature for 800 hours with corrosion potential and aspect monitoring and salt mist test (in accordance with CEI 68-2-11, Ka method) for 240 hours for at least 3 specimens (70 × 35 mm) of each variant, with intermediary examinations after 24, 48, 72, 144, 168, 192 and 240 conditioning hours.

RESULTS AND DISCUSSION

Usually, conversion coatings formation represents a controlled corrosion reaction of the substrate, as a result of equilibrium established between the native oxide dissolution and coating growth that prevents further the solution ingress. Due to the fact that it is an electrochemical process in nature, the use of electrochemical measurement techniques to monitor the conversion process appeared to be useful. There are several studies that already showed the value of recording of open circuit potential of Al electrode during chemical conversion, mainly in the case of chromate layers [23].

To form hydrotalcite type coatings, Al specimens have been immersed in conversion solution having the composition mentioned above and a strong hydrogen evolution is noticed, especially in the early moments of the process. According as more specimens are subjected to conversion in the same bath, the time up to hydrogen evolution ceased was diminished, in close correlation with the amount of dissolved aluminium. Variation of open circuit potential, U_{oc} with immersion time for an Al substrate as shown in Figure 1, clearly evidence the evolution of conversion process, for various

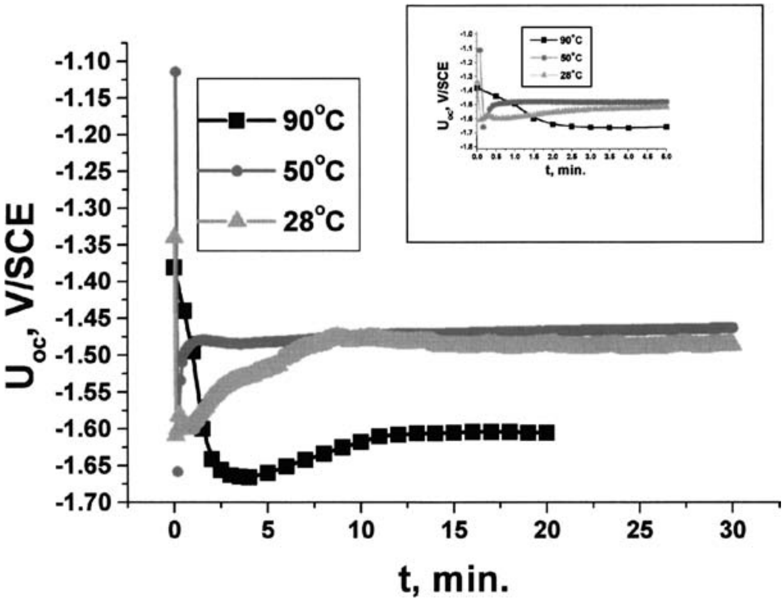


FIGURE 1 Evolution of open circuit potential vs. conversion time for HT film formation at various operating temperatures.

values of operating temperature. It can be seen that U_{oc} decreased in the first seconds of immersion, due to metal dissolution in the strong alkaline solution, associated with H_2 evolution from the surface. After a certain period, depending on the applied temperature, U_{oc} started to increase when the conversion film forms up to a quite stable value, assigned to thickening of the coating and gas evolution ceased. The general shape of U_{oc} recordings is quite similar, regardless the applied solution temperature. However it should be noticed that slightly more positive values for the stable open circuit potential are attained at temperatures up to 60°C; then it shifts towards relatively electronegative ones in close correlation with gas evolution intensity.

If U_{oc} evolution for successive metallic specimen immersion in the same bath is followed (that implies higher dissolved aluminium in the solution), an increase of the stable potential was noticed toward positive direction and also a shortening of gas evolution period. This finding supports the idea that to facilitate the growth rate of conversion coating, a certain amount of aluminium should be present in the bath to assure the precipitation or nucleation and subsequently formation of hydrotalcite type coating on the metallic surface [18].

The conversion process has been also simultaneously evaluated quantitatively through determination of the coating ratio R, defined as the ratio of the weight of the HT coating to the weight of dissolved aluminium, as exemplified in Figure 2. The lowest value of R is obviously met in the first minutes of conversion, when strong hydrogen evolution takes place and a large amount of Al is dissolved, indicated also by the value of open circuit that abruptly moves towards the most electronegative values. When the coating starts to form, R increases up to a quasi-stable value and this process is also easily identified in the potential evolution towards positive direction.

Thus, it should be concluded that the potential of Al electrode during chemical conversion process is a sensitive tool to evaluate the changes on the surface and in chemistry of solution.

Usually, these HT type conversion coatings exhibit a porous structure and a whitish, slightly mat appearance, with coating mass of about $1200\,\mathrm{mg/m^2}$.

To increase protective action of such kinds of films, a second step was applied involving Ce(III) or Mn(VII) based solutions, to seal the pores. The monitoring of open circuit potential in time during this subsequent treatment was again recorded as an indicator of sealing efficiency, as it is presented in Figure 3. As it can be noticed from this figure, U_{oc} evolution depends on the used solution type.

Thus, when sealing process involves Ce(III) solution, U_{oc} moves in negative direction in the first seconds of immersion, suggesting initial species

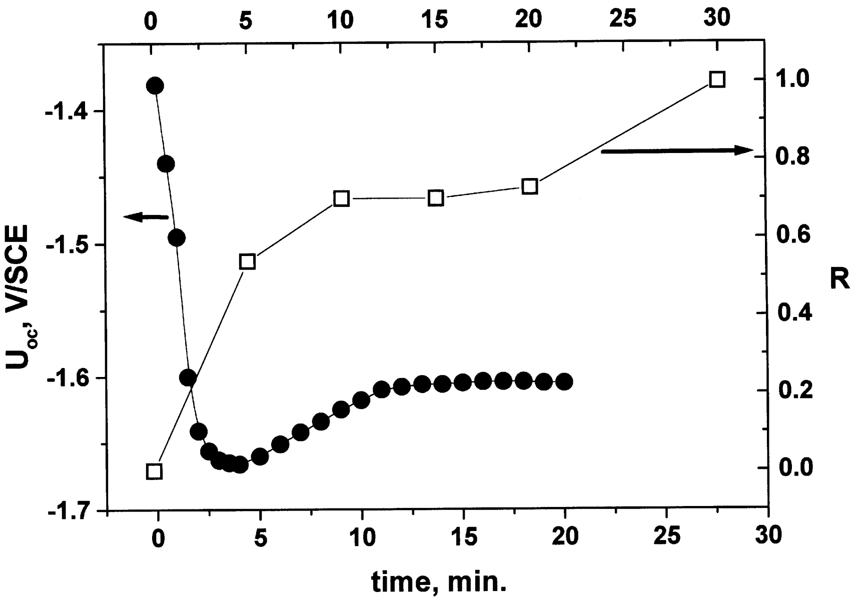


FIGURE 2 Dependence of open circuit potential and coating ration vs. immersion time for HT film formation at 90°C temperature.

absorption on the surface. Then, potential increases to more positive values, up to a quite stable value, as protective second layer is formed.

On the surface, the reduction of oxygen also occurs (Eq. (1)) that leads to OH^- formation [9].

$$O_2 + 2H_2O + 4e^- \Rightarrow 4OH^- \tag{1}$$

Further reaction of Ce^{3+} with hydroxide ions can lead to formation of protective cerium oxide (Eq. (2)) that entirely covers the surface, also facilitated by the alkaline pH of HT coating [9].

$$2Ce^{3+} + 4OH^- + O_2 + 2e^- \Rightarrow 2CeO_2 + 2H_2O \tag{2}$$

When the second step involves $KMnO_4$ solution, U_{oc} shape is characteristic to the presence of a strong oxidant anion that facilitates an additional oxidation. Thus, after an initial decrease, the potential moves with a large slope towards more electropositive values up to 4–5 minutes of immersion, followed by a lower increase but in positive direction, too, up to the end of the process. The coating exhibits a golden-yellow colour that can indicate the presence of manganese oxides, as result of Mn(VII) reduction reaction on the surface [16].

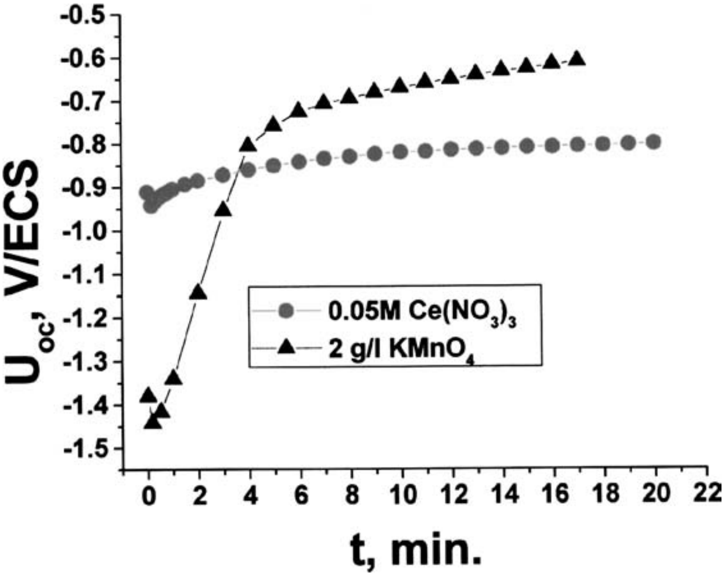


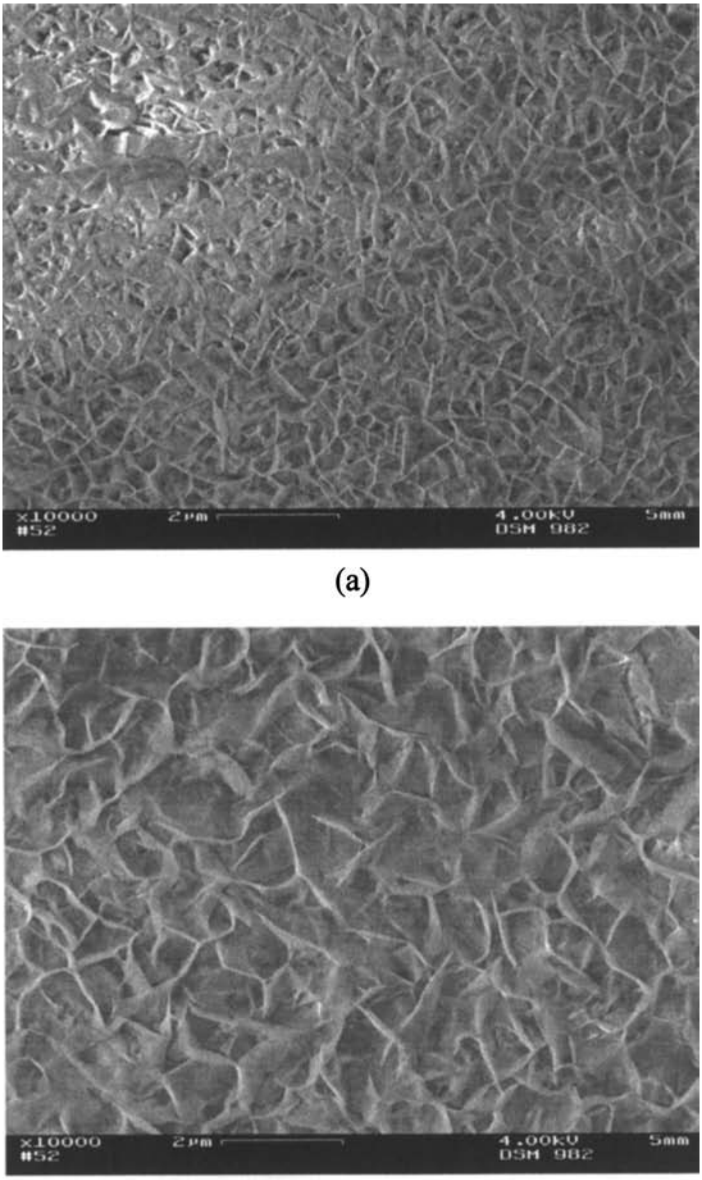
FIGURE 3 Evolution of open circuit potential vs. conversion time for HT modified coatings through a second sealing step in Ce (III), Mn (VII) based solutions.

SEM pictures revealed uniform HT conversion layers, that entirely cover the metallic surface, being formed by crystallites having about 200–300 nm walls length and average pore size of approximately 200–400 nm, as shown in Figure 4.

The second step in $Ce(NO_3)_3$ or $KMnO_4$ solution facilitates the sealing of the pores, so that the bare metal is not in direct contact with environment. It should be noticed that these HT thin layers offer a nanodimensional porous architecture quite similar to that obtained through sol-gel technique [24]. EDX analysis revealed the presence of aluminium, oxygen, but did not detect the presence of Li, Ce or Mn, that may be due to the fact that this technique is sensitive if the elements are present above 0.4% by weight.

To evaluate corrosion resistance of HTCCs on various Al substrates, polarisation curves have been recorded in 0.5 M NaCl, for pure Al foils and AU4G1 alloy type, in one and two step procedures, as it can be seen in Figures 5 and 6.

As a general trend, HTCCs shift pitting potential towards electropositive direction with about 100 mV both for Al foils and alloys. The presence of HT type coatings lowers reduction reaction kinetics and the overall result determines a diminished corrosion current that attains values 10 times lower than in the case of non-treated bare metals. Thus values of corrosion



(a)

(b)

FIGURE 4 SEM micrographs for HT modified coatings: (a) HT-Mn; (b) HT-Ce.

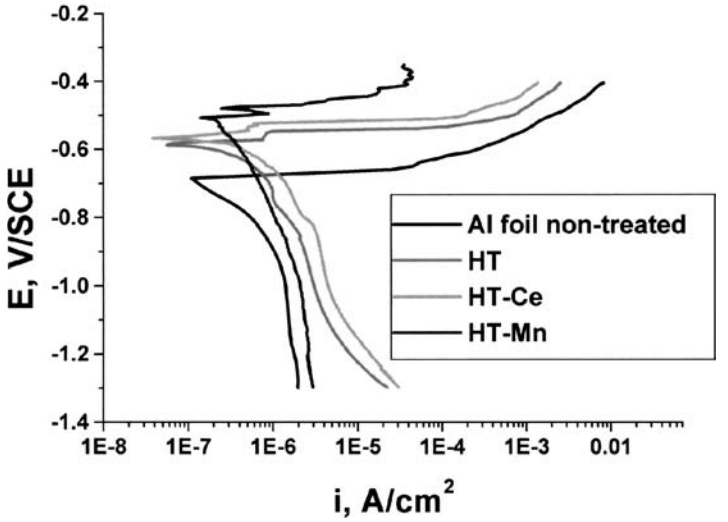


FIGURE 5 Polarization curves in semilogarithmic coordinates for Al foils (99.5% Al purity) non-treated and coated with HT type modified films.

currents of about 1 $\mu A/cm^2$ for bare metal and of 0.1–0.2 $\mu A/cm^2$ for coated one have been determined.

The second step based on Ce(III) salts revealed a better corrosion protection comparatively with $KMnO_4$ based one, as it can be noticed from

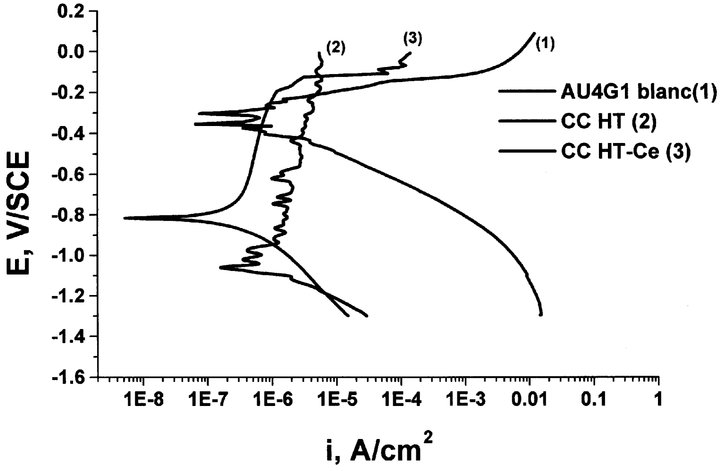


FIGURE 6 Polarization curves in semilogarithmic coordinates for Al alloy of AU4G1 type, non-treated and coated with HT type modified films.

evaluation of penetration index, too, as presented in Figure 7. The low values comparatively with those found in the literature should be due to the involved Al base metal, respectively of high purity (99.5) [14,20].

Corrosion potential monitoring during continuous immersion in 0.5 M NaCl, as it can be seen in Figure 8, revealed again the good influence of the second sealing step on the protective characteristics of these coating

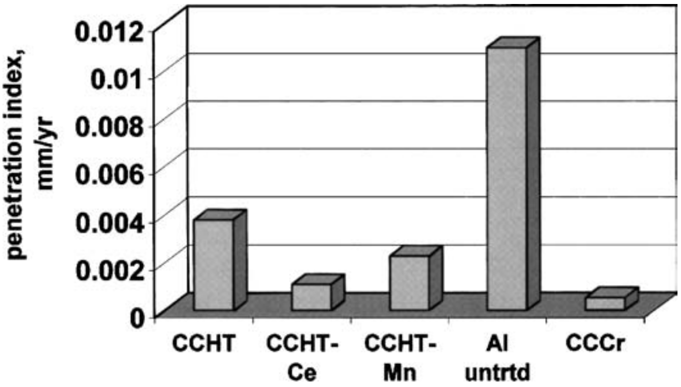


FIGURE 7 Corrosion rate, expressed as mm/year, for HTCCs chemical conversion coatings.

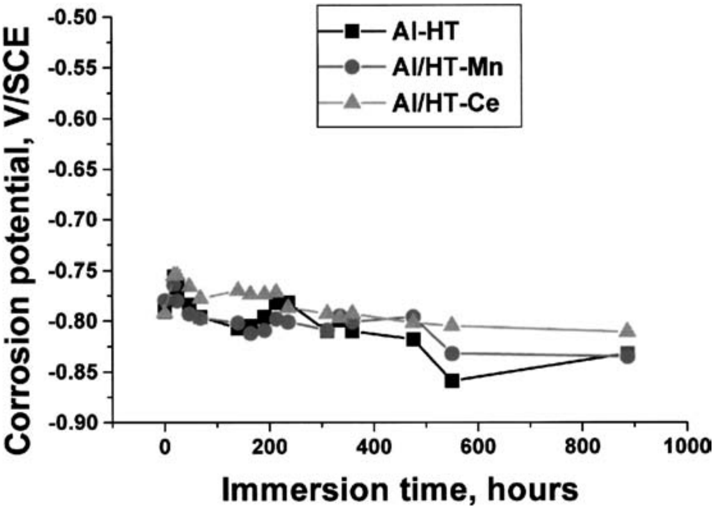


FIGURE 8 Corrosion potential evolution during continuous immersion in 0.5 M NaCl solution (Al foil as metallic substrate).

layers, especially that based on Ce salts, phenomenon that is in accordance with other literature information that highlights the beneficial influence of lanthanides, mainly Ce on the further anticorrosive resistance in aggressive environments [14,16,17].

As Figure 8 shows, corrosion potential slightly moves towards more electropositive values during the first 24 hours of immersion, an indicative of the protective effect of the coating; then, a decrease of potential is noticed, more evidenced for Al-HT systems.

Al/HT-Ce achieved the highest corrosion potential value after 900 hours of immersion and just few fine pits per dm^2 have been evidenced.

The same very good behaviour and evolution against chloride aggressive environments has been revealed during salt mist test for 240 hours, as is briefly presented in Figure 9, for Al alloys specimens coated with HT type conversion films. It should be mentioned that this type of base material has been selected because it is currently used in industrial applications, especially in aviation industry.

Thus, in the case of HT-Ce system after 240 conditioning hours just few numbers of fine pit spots appeared, usually located in the hole region and substrate defects. For HT-Mn coatings a slight rinse of yellow passive film has been noticed after 192 hours of salt mist. Usually a protective conversion coating should pass 168 hours of salt mist test with little or no pitting appearance, according to AST B117 standard. According with this requirement and the experimental results described above, it should be considered that hydrotalcite type coatings may be taken into consideration as viable alternatives to chromate ones, being able to assure at least a comparable corrosion protection.

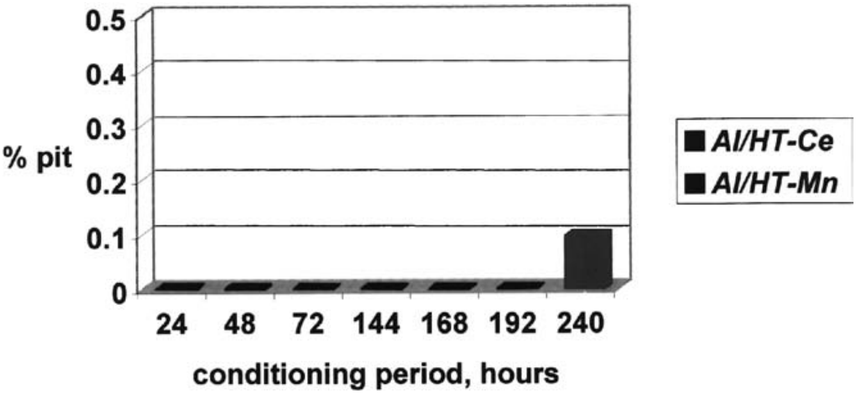


FIGURE 9 Evolution of pitting appearance on Al alloy substrates coated with HT type modified coatings during salt mist test.

CONCLUSIONS

According to the experiments that have been performed it should be conclude that:

- conversion coatings based on lithium-aluminium hydroxides offer an anticorrosive protection to Al and Al alloys metallic substrates;
- it has been evidenced a synergetic effect of two-step procedures, such as: HT-Ce, HT-Mn, materialised by a halving of corrosion current and E_{pit} increase by about 100 mV;
- the best corrosion protection was evidenced in the order:

$$\text{Al/HT-Ce} \cong \text{Al/HT-Mn} > \text{Al/HT}$$

- The obtained results recommend these conversion coatings as potential replaces of chromate ones at industrial level, mainly for normal exploitation conditions and temperate climate. Further investigations will be performed, for a better understanding of conversion mechanism and to establish an industrially compliant technological process.

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