Chromium-free conversion coatings based on inorganic salts (Zr/Ti/Mn/Mo) for aluminum alloys used in aircraft applications

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ABSTRACT

Novel chromium-free conversion coatings based on Zr/Ti/Mn/Mo compounds were developed at a pilot scale to improve the corrosion resistance of the AA2024-T3 and AA7075-T6 aluminum alloys for aircraft applications. The influence of the presence of Zr and Ti in the Zr/Ti/Mn/Mo conversion bath's formulation on the corrosion resistance of the coated alloys was investigated. The corrosion resistance provided by the conversion coatings was evaluated by salt spray exposure and potentiodynamic sweeps. Optical and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS) and atomic force microscopy (AFM) operating in the Kelvin probe mode (SKPFM) were used to provide microstructural information of the coated samples that achieved the best results in the corrosion tests. The salt spray test evidenced the higher corrosion resistance of the coated samples compared to the bare surfaces for both alloys. The potentiodynamic tests showed that the corrosion current density decreased for coated AA7075-T6 and AA2024-T3 alloys, which indicated an obvious improvement of the corrosion resistance with all the processes for both alloys. Although the corrosion resistance of the coated samples appeared to be higher for the alloy AA7075-T6 than for the alloy AA2024-T3, both alloys achieved the best corrosion protection with the coatings deposited from conversion bath formulations containing no titanium salts. The microscopy analysis on the coated AA7075-T6 samples revealed that a local deposition of Zr compounds and, possibly, an oxidation process occurred in the vicinity of the alloy's intermetallic particles. The amount of the Zr deposits at these locations increased with coating's formulations without Ti, which provided the best corrosion resistance.

The Cr-free conversion coatings developed in this study for the AA7075-T6 and AA2024-T3 alloys do not meet yet the strict requirements of the aircraft industry. However, they significantly improved the corrosion performance with respect to the bare alloys and could be a good starting point for further studies and optimization.

Keywords

Chromium-free conversion coatings, aluminum alloys, corrosion protection, salt spray test, AFM/SKPFM, aeronautics.

1. Introduction

High strength aluminum alloys are employed by the aircraft industry as structural materials due to the combination of their valuable mechanical properties and strength to weight ratio [1]. Unfortunately, the presence of some alloying elements, such as copper, magnesium, zinc, manganese, silicon or iron, results in the formation of coarse intermetallic particles during casting and homogenization. From an electrochemical standpoint, copper and zinc-rich intermetallics are cathodic to the aluminum matrix, hence promoting the dissolution of aluminum, while the magnesium-rich intermetallics are anodic to the aluminum matrix and undergo dissolution. This mechanism favors the occurrence of localized corrosion, such as pitting, affecting the performance of the AA2024-T3 and AA7075-T6 alloys which are two of the aluminum alloys that are most commonly used in aeronautical applications [2].

Chromate conversion coatings (CCC) have been extensively used as anticorrosive treatments in the aircraft industry for over 50 years because of their self-healing ability and active corrosion protection [3,4]. Labile Cr (VI) can be released from the coating and migrate to a damaged region where its electrochemical reduction to Cr (III) may occur, protecting the aluminum alloy surface from further corrosion [5]. Despite their undeniable performance and advantages, such conversion treatments need to be replaced by more environmentally friendly alternatives since Cr (VI) has been reported to be highly toxic and carcinogenic and provokes effluent disposal problems [6]. The United States Environmental Protection Agency (EPA) classifies the Cr (VI) as a Group A known human carcinogen. Furthermore, although the aerospace industry is still exempt for obvious safety concerns related to corrosion, Cr (VI) is regulated by the European directives 2000/53/EC and 2002/95/EC for the automotive and electronics sector, respectively.

Numerous alternative non-chromate conversion coatings based on elements with a similar chemistry to that of chromium have been studied. The inorganic species considered for Cr (VI) replacement can be divided into the following categories: 1) Reducible hypervalent transition metals (compounds of Mo, Mn, V, Tc). Like Cr, the highvalent oxoanions of these elements exist in aqueous solution. 2) Difficult-to-reduce transition metal oxides (Zr, Ti, Y,

Hf, Ta) and covalent oxides (oxides and mixed oxides of Si, Ge, P, Te) and 3) Precipitated coatings including rare-earth metals (REM) and boehmite and hydrotalcite coatings [7].

Molybdenum is a well-known corrosion inhibitor when present in the electrolyte as Mo (VI) [8-10], and manganese exhibits chemical similarities (structural and electronic) to chromium [11]. Both elements have an oxidizing behavior that can reinforce the natural oxide of the alloy. Moreover, their anions, which are highly soluble, undergo reduction to insoluble products that could provide an extra-protection for the oxidized surface by precipitation. Elements such as Ti, Zr, Nb, Hf, and Ta form very stable oxides in their highest oxidation state. Peroxo complexes and acid fluorides of Zr, Ti, Nb, and Hf exist at low pH. As a consequence, zirconium and titanium compounds have also gained acceptance as corrosion inhibitors and baths containing compounds such as fluorides of zirconium and titanium have been used in the past to develop chromium-free conversion coatings for aluminum alloys [12,13].

Different authors studied the mechanism of corrosion inhibition of rare earths compounds and in particular of cerium species [14,15]. Several studies evidenced that the microstructure of aluminum alloys played a very important role on the corrosion behavior and inhibition [16,17]. In the case of the cerium-based coatings, an increase in pH occurs at the cathodic intermetallic particles due to chemical reactions, which lead to the precipitation of the cerium hydroxides. Hence, the preferential deposition of the cerium containing layer on top of the cathodic intermetallics is reported in several investigations [18-20].

Some of these treatments based on non-chromate conversion coatings have been already identified or even commercialized over the last decade for several industrial applications. Nevertheless, none of them provides sufficient corrosion protection to the aluminum substrates to meet the stringent aeronautical requirements for specific applications [21,22] and the replacement of hexavalent chromium based conversion coatings is still found as one of the main topics at international conferences in the aeronautic sector such as SURFAIR and IntAIRCOAT. Indeed, the aircraft industry has to comply with the EU REACH regulation that establishes the latest application date of Cr (VI), currently expected at 2016/2017 [23]. Therefore, environmentally acceptable alternatives to chromate conversion coatings that

exhibit comparable corrosion protection to the chromate coatings are still needed for the aircraft industry since none of the available alternatives comply with all the requirements and corrosion of structural alloys poses a great safety concern in this application. Other structural alloys with enhanced corrosion resistance with respect to the AA 2024-T3 and AA7075-T6 are also being investigated in parallel but these will also need Cr-free conversion coatings and primers.

In the current study, novel chemical conversion coatings were developed, characterized and evaluated in terms of corrosion resistance for the protection of the AA2024-T3 and AA7075-T6 aluminum alloys, as an alternative to chromium (VI)-based treatments for aircraft applications, leading to an enhanced corrosion resistance of both AA2024-T3 and AA7075-T6 compared to the bare alloys. The conversion baths were environmentally friendly aqueous formulations based on Zr/Ti/Mn/Mo compounds. While other environmentally-friendly coatings that have been reported involve processes with a post-treatment like sealing [24] or a heating step after the conversion coating [25, 26] or heating of the conversion baths [10], these coatings were developed in a single-step process after the pretreatment, by immersion of the panels in the conversion baths at room temperature and for times between 2 and 4 minutes. In addition to the efficient corrosion protection required to the coatings, these aspects should be considered for the industrial application of the processes, which should be easily implemented in a traditional tank process with no investment or need of longer process periods.

Aluminum panels of both AA 2024-T3 and AA7075-T6 alloys were treated by immersion in the chromium-free conversion baths based on Zr/Ti/Mn/Mo compounds. A preliminary study was carried out to evaluate the influence of the chemical conversion coatings process parameters on the corrosion resistance using Statistical Design of Experiments (DoE) methodology, based on STATGRAPHICS PLUS v5.1 software.

Based on the results obtained with the DoE, several aqueous solutions of Zr/Ti/Mn/Mo compounds were used to develop the different chromium-free conversion coatings at a pilot scale. The corrosion protection offered by these coatings was evaluated by salt spray exposure, electrochemical methods (potentiodynamic sweeps) and by Scanning Kelvin probe

force microscopy (SKPFM). Besides, optical microscopy and scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) were used to provide complementary microstructural information.

2. Experimental

2.1. Materials

AA2024-T3 and AA7075-T6 aluminum alloy substrates with different shapes and sizes were used depending on the characterization method that the coatings would be subjected to: panels (250x75x1 mm) for salt spray exposure tests and SEM/EDS analysis; discs (16 mm in diameter) grinded to 600 grit for electrochemical tests; discs (16 mm in diameter) polished with 1µm diamond abrasive for Scanning Kelvin Probe analysis. Table I shows the percentage weight composition of the selected alloys.

Potassium hexafluorozirconate (K_2ZrF_6), sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$), potassium hexafluorotitanate (K_2TiF_6) and potassium permanganate ($KMnO_4$) salts were obtained from Aldrich. To prepare the conversion baths, these salts were dissolved in deionised water. A hexafluorozirconic acid solution (H_2ZrF_6) 50wt% in H_2O from Aldrich was used to adjust their pH. The solutions were used within 24 hours after preparation.

The commercial solutions Turco 4215NCLT and Turco Smut Go NC were acquired from TURCO ESPAÑOLA S.A. for the pretreatment of the aluminum alloys prior to the conversion coating deposition.

2.2. Preliminary study based on statistical design of experiment (DoE) methodology

In order to evaluate the effect of the key parameters on the corrosion resistance of the coatings, the DoE methodology based on STATGRAPHICS PLUS v5.1 software was used. The DOE methodology provides the design of a matrix of experiments in order to determine the individual and interactive effects of the key parameters that could affect the output results, in the present case, the corrosion resistance of the coated samples.

The studied parameters were the conversion bath's pH (2, 3.5 and 5), the conversion bath's temperature (20, 40 and 60°C), the immersion time (2, 3 and 4 minutes) and the concentration of active species Zr (4 and 8 g/l of K_2ZrF_6), Ti (2, 6 and 10 g/l of K_2TiF_6), Mo (10, 20 and 30 g/l of $Na_2MoO_4 \cdot 2H_2O$) and Mn (2, 15 and 30 g/l of $KMnO_4$) in the conversion bath. A matrix of experiments was defined by the DoE software according to those values and different

conversion coatings were deposited on both the AA2024-T3 and AA7075-T6 aluminum alloys.

The corrosion resistance of each coated sample was evaluated after 168 hours of exposure in a salt spray chamber following the indications of the MIL81706B standard. Based on the results of this evaluation, the DoE methodology provided a mathematical model corresponding to the corrosion performance within the range of the studied parameters for both the AA2024-T3 and AA7075-T6 alloys.

2.3. Chromium-free conversion coatings

Based on the preliminary study, four different chromium-free conversion coatings were deposited onto panels of the AA 2024-T3 and AA7075-T6 alloys. The content of the Ti and Zr salts in the conversion bath was varied, while the concentration of Mo and Mn salts was 20g/l each (see process conditions in Table II). The conversion bath's pH and temperature were fixed at 5 and 20°C, respectively.

As-received aluminum alloy samples were pre-treated according to commercial procedures used in the aerospace industry: degreasing with acetone, alkaline cleaning with Turco 4215NCLT and finally, deoxidizing with Turco smut Go NC.

The conversion coatings were then formed by immersing the pre-treated aluminum alloys panels for 3 minutes in the different bath formulations (see Table II), at 20°C without stirring. The treated samples were finally dried in air for 24 hours and stored in a dry atmosphere before their characterization.

2.4. Characterization methods

In the aeronautical sector, the corrosion resistance of the conversion coatings is routinely evaluated by the salt spray test. In the current work, the corrosion resistance of the coated aluminum alloys was firstly studied by the salt spray test following the indications of the MIL81706B aeronautical standard. Additional electrochemical tests were also performed to further evaluate the coatings corrosion resistance. Later on, the morphology and the chemical composition of the surface and the surface's volta potential were studied for the coated

samples that best performed in terms of corrosion resistance in order to relate these properties with their corrosion resistance. The methods are described below.

The corrosion resistance of the coatings deposited onto both alloys was evaluated by salt spray test (SST) following the indications of the MIL81706B aeronautical standard (samples subjected to a 5% salt spray test in accordance with the ASTM-B117 standard, except that the surface of the panels was inclined 6 degrees from the vertical). The salt spray tests were conducted in C&W/SF-1000-CCT salt spray chamber for 168 hours. Bare (non-coated) substrates and panels treated with a chromate conversion process certified for aeronautic applications (Alodine 1200S) were also tested as reference. The samples were comparatively evaluated after the tests.

The corrosion resistance was also evaluated by electrochemical tests. The electrochemical measurements were carried out with SOLARTRON 1286 potentiostat/galvanostat. The tests were based on the ASTM G5 and ASTM G61 standards. A conventional three-electrode cell with a platinum counter electrode and Ag/AgCl reference electrode was used for all the electrochemical tests. The grinded discs were inserted in a sample holder exposing 1 cm² of the surface. Particular attention was taken during the installation of the samples in the holder to avoid any crevice corrosion or other localized damage of the coatings. The corrosion behavior of the samples was evaluated using potentiodynamic sweeps, which started when the Open Circuit Potential reached a pseudo-stable value. During the potentiodynamic tests, the samples were immersed into a 0.1M Na₂SO₄ + 5mM NaCl solution in the case of AA2024-T3 alloy and into a 0.1M Na₂SO₄ + 10mM NaCl solution in the case of AA7075-T6 alloy. Due to the higher corrosion susceptibility of the AA2024-T3 alloy, the test solution for this alloy had a lower content of chlorides so that differences in the corrosion performance could be easily observed amongst the different conversion coatings; if the test solution is too corrosive for the alloy under study, corrosion might occur so rapidly that differences among the distinct samples are not clearly noticeable. The test conditions were: sweep range -1.0 V to a potential more anodic than pitting potential (to be sure to observe the pitting potential), sweep rate 40 mV/min and air exposure 23 ± 2 °C without agitation. Bare substrates were also electrochemically tested as reference.

The salt spray tests and the electrochemical measurements can give complementary information, even if the results may not be totally in perfect accord. The salt spray test is a “long term test” (168h of exposure in the present case), known as a very aggressive artificial ageing process. On the other hand, the electrochemical tests are performed for a short time (<24h) by immersion in an aqueous solution, which is usually considered as a milder ageing environment. The electrochemical measurements give “instantaneous” information about the corrosion mechanisms at the moment of the measurement while the salt spray test considers the full ageing time.

The morphology and the chemical composition of the surface of the coated panels were assessed by optical microscopy (Reichert MEF 3) and scanning electron microscopy (SEM, JEOL JSM 5910 LV) coupled with an energy dispersive X-ray (EDS) analyser (INCA).

Atomic force microscopy (AFM) operating in the Kelvin Probe mode (SKPFM) was used to measure the bare aluminum and the coating's surface volta potentials and to study the influence of the conversion treatment on the surface volta potential difference between the aluminum matrix and the intermetallics.

3. Results and discussion

3.1. Preliminary results (DoE processes)

AA2024-T3 and AA7075-T6 aluminum alloy panels were treated with the conversion processes of the matrix defined by the DoE software. The corrosion resistance of each coated sample was evaluated after 168 hours of exposure in the salt spray chamber. Based on this evaluation, a mathematical model (see Table III) corresponding to the corrosion performance within the range of the studied parameters was provided by the software used for the DoE methodology for both alloys. In both cases, the results showed that the resistance of the coating depended mainly on the pH of the chemical conversion bath: the higher the pH, the higher the corrosion resistance of the coating. The model gave a better fit ($R^2 = 83.58\%$) for the AA7075-T6 alloy in terms of corrosion resistance. For this alloy, the “number of pits” depended linearly on the Mn concentration and on the pH of bath. However, the influence of the pH was also dependent on the Mo concentration ($\text{pH} \times [\text{Mo}]$). Other factors affecting the corrosion performance were the binary interactions $[\text{Mn}] \times \text{Time}$, $[\text{Ti}] \times [\text{Zr}]$ and $[\text{Zr}] \times [\text{Mn}]$, and the quadratics Time, $[\text{Ti}]$ and $[\text{Mo}]$. In the case of the AA2024-T3 alloy, the corrosion performance was affected by the binary interactions Temperature $\times$ pH, $[\text{Ti}] \times [\text{Mn}]$ and the quadratics Temperature, Time, $[\text{Ti}]$ and $[\text{Mn}]$. For the two alloys, the results showed that the best corrosion resistance was achieved with pH and temperature values of 5 and 20°C, respectively.

3.2. Characterization of the chromium-free conversion coatings

3.2.1. Corrosion tests

Salt Spray Tests

Visual observation of the samples treated with the different conversion processes after 168 hours of exposure in the salt spray chamber showed that the qualitative behavior of both alloys was similar, although, quantitatively, the number of pits was significantly lower in the AA7075-T6 alloy. This was expected due to the higher Cu content of the AA2024-T3 alloy. Figures 1 and 2 show the general appearance of the tested surfaces for the AA2024-T3 and AA7075-T6 alloys, respectively.

Bare panels showed general corrosion after the salt spray exposure. On the contrary, panels treated with the Alodine 1200S chromate conversion process did not show any signs of corrosion.

All the panels treated with the new conversion coating processes showed corrosion pits on the surface. However, comparing with the bare substrates, all the conversion coatings improved the corrosion resistance for both aluminum alloys.

Panels coated with processes 1 and 4 (see details in table II) exhibited numerous pits and corrosion products on the whole surface. Both the number of pits and the corrosion products decreased for panels coated with processes 2 and 3 and, particularly, the AA7075-T6 alloy treated with process 2 showed the best corrosion resistance behavior and the lowest number of pits amongst all the tested coatings.

Both processes 2 and 3 were free from Ti; in the case of process 2, Zr, Mo and Mn salts were amongst the bath constituents and in the case of process 3, Mo and Mn salts. These results indicated that the formulations free from titanium salts but comprising the zirconium compounds (from the Zr salt and/or from the hexafluorozirconic acid used to adjust the pH) together with the Mo and Mn salts led to increased protective ability on the aluminum alloys.

Electrochemical Tests

Figure 3 shows the potentiodynamic curves for the four conversion processes for both alloys. The results of the Tafel analysis were studied (Table IV and Figure 4): corrosion potential (E_{corr}), pitting potential (E_{pit}), differences between the corrosion and the pitting potentials ($E_{corr} - E_{pit}$), corrosion current density (j_{corr}), anodic and cathodic Tafel slopes (β_a and β_c , respectively). Then the polarization resistance (R_p) was calculated using the following formula:

$$R_p = (\beta_a \beta_c) / (2.303 (\beta_a + \beta_c) j_{corr})$$

In all cases, the conversion coatings shifted the corrosion potential (E_{corr}) towards more negative values with respect to the bare aluminum alloys (Figure 3), indicating a possible sacrificial effect towards the bare alloy.

In the case of the bare alloys, the difference $E_{pit} - E_{corr}$ close to 0 (Table IV and Figure 4a) indicates that the materials naturally pit when exposed to the test environments. All the conversion processes shifted E_{pit} to less negative values for the AA7075-T6 alloy, which means an improvement of the corrosion protection, whereas all conversion processes, with the exception of process 3, slightly shifted E_{pit} to more negative values for the AA2024-T3 alloy. Nevertheless, the main influence of the conversion process on the polarization curves, compared to the untreated aluminum alloy, is the presence of a plateau on the anodic branch indicating a passive behavior. That means that the coated materials will not pit at least until being exposed for some time to the testing environments while the bare alloys is susceptible to pit as soon as it is exposed to the test environment.

The corrosion current density (j_{corr}), shown for all processes in Table IV and Figure 4b, is one other important parameter for the corrosion assessment. The j_{corr} values for AA7075-T6 were less than 1 A/cm^2 , one order of magnitude lower than the bare alloy, with all the processes 1-4. In the same way, AA2024-T3 alloy treated with processes 2 and 4 led to a decrease of j_{corr} in one order of magnitude (values less than 1 A/cm^2). In a previous study, G. Yoganandan et al. considered a decrease of the corrosion current density below 1 A/cm^2 as an indication of the efficiency of the coatings [27] .

The j_{corr} can be directly related to the corrosion rate and the efficiency of the process:

$$Efficiency (\%) = 100 \times [(j_{corr_{uncoated\ alloy}} - j_{corr_{coated\ alloy}}) / j_{corr_{uncoated\ alloy}}]$$

For the AA2024-T3, the efficiency of the conversion processes was relatively poor (less than 70% for the best one, process 2 - see Table IV and Figure 4c). For the AA7075-T6, all the processes decreased the corrosion rate and had a better efficiency (around 85% in average, and 90% for the best one, process 2 – see Table IV and Figure 4c).

For both aluminum alloys, there was an important difference between the bare alloys and the alloys treated with the conversion coating processes: in both cases, the comparison between the curves of the bare alloys and the coated alloys show a strong increase of β_a (Table IV) for the coated one indicating a pitting behavior for the bare alloys and a passive behavior for the coated one. Moreover, the strong decrease of β_c for the 7075-T6 alloy (Table IV) pointed towards a change from oxygen diffusion (limiting step due to pitting) to a charge transfer limitation (oxygen reduction).

The calculation of the polarization resistance (Table IV and Figure 4d), integrating both the corrosion current density and the anodic and cathodic processes using β_a and β_c , is a robust way to assess the improvement of the corrosion behavior given by the conversion coating. In all the cases, an improvement was observed. In the case of the AA2024-T3, R_p gained one order of magnitude with the conversion coatings (the best result being obtained by the process 2). On the AA7075-T6, the improvement of the corrosion behavior due to the conversion coatings is more significant since R_p gained 2 orders of magnitude (the maximum polarization resistance being obtained by the process 2).

Figure 5 shows the surface's morphology of pitted samples for the bare AA7075-T6 alloy and the AA7075-T6 alloy treated with conversion process 2. Figures 5a and 5b suggest that the macro pits form through coalescence of micro pits. Figure 5c shows the SEM image of a pit and Figure 5d shows an EDS spectrum taken inside the pit. The germination area of the pit seems to be related to a copper-containing particle. Zr and Mn are present in the pitted area. This is in agreement with the literature in which other studies concerning chromate

conversion coatings confirm that the deterioration of the coatings during exposure to aggressive environments starts at the location of the intermetallics [3].

Both salt spray test and electrochemical measurements showed that the best results on both alloys were obtained with the conversion process 2, which had Zr, Mo and Mn, but no Ti.

3.2.2. Surface morphology and composition of the coated panels

Since, as expected, the corrosion resistance of the coated panels was significantly lower for the alloy AA2024-T3 than for the alloy AA7075-T6, surface morphology and composition was only studied for the AA7075-T6 samples in order to relate the composition of the conversion bath formulations with the structure, morphology and composition of the coated surfaces.

The surface morphology of the AA7075-T6 panels treated with processes 2 and 3 (processes with formulations free from Ti; see details in Table II) was an “almost clean” surface with only very few roughly spherical particles on top (see Figure 6a for panels treated with the process 2), while the processes containing Ti (processes 1 and 4) led to more of these particles on the panels surface, particularly the process 4 which contained the highest content of titanium salt (Figure 6b). Figures 6c and 6d show the EDS spectra of the roughly spherical deposits on samples treated with processes 2 and 4, respectively, which seemed to be composed of oxides, hydroxides and/or fluorides of the inorganic elements (Ti, Zr, Mo, Mn). The surface composition outside the spherical deposits was uniform and similar to the bare (non-coated) substrate for all the panels treated with the different conversion coating processes. This indicated that the deposited coatings were mainly based on the formation of salt deposits on the aluminum surface.

A closer view of the flat surface of the AA7075-T6 alloy treated with processes 2 and 4 at a higher magnification (Figures 6e and 6f, respectively) evidenced a local deposition and, possibly, an oxidation process at the intermetallic (IM) particles. This oxidation process could occur due to the oxidizing properties of both Mn and Mo, which was already mentioned in the introduction section. The surface morphology at the IM particles was different depending on whether or not there was Ti in the conversion bath. On the surface of the coatings without Ti

(processes 2 and 3), there were amorphous deposits completely covering some intermetallic particles (Figure 6e) while for the coating formulations containing Ti (processes 1 and 4), the intermetallic particles were covered by aggregated spherical particles (salt deposits) (Figure 6f).

The EDS analysis at the intermetallic particles (see Table V) showed the presence of Mo/Mn/Zr/Ti species, as well as the K and F elements (also present in the conversion baths), while no elements from the conversion baths were detected on the alloy matrix. Therefore, preferential deposition/oxidation processes occurred in the vicinity of the intermetallic particles.

It is well-known that the microstructure and morphology of the surface of the aluminum alloy affect the nucleation and growth of the conversion coatings as well as their protective properties. Preferential deposition of Zr and Ti compounds on and around intermetallic particles was also observed previously for conversion coatings on the AA6060 alloy [27]. The deposition seemed to be related to the local alkalization at the intermetallics due to oxygen reduction and hydrogen evolution, i.e., controlled by local pH variations [28]. This mechanism is similar to the one described for the rare earth conversion coatings. The deposition extent was reported to vary considerably depending on the alloy due to the intermetallics, their size and distribution.

In the case of permanganate, studies concluded that the MnO_2 deposits over the Cu-rich intermetallics present on the AA2024-T3 alloy were driven by their cathodicity with respect to the alloy matrix and involving a redox reaction [27].

This deposition mechanism is similar to that of the chromate conversion coatings, but different from Zr and Ti based conversion coatings. In the case of the chromate conversion coatings on the AA2024-T3 alloy, the intermetallics have been reported as preferential nucleation sites for the film formation; they act as cathodic sites and enable the chromate reduction reaction [3]. However, the formation of the chromate conversion film continues afterwards on the matrix, and the driving force that causes the deposition of the layer preferentially on top of the intermetallics ceases.

On the other hand, the semiquantitative EDS analysis on the intermetallic particles for the panels treated with the different processes (see Table V) showed that the Zr percentage in the local deposits/oxides were higher in coatings without Ti (processes 2 and 3), even when the presence of Zr in the bath came from the hexafluorozirconic acid, used to adjust the pH, and no Zr salt was added.

3.2.3. Influence of conversion treatments on surface volta potentials

The identification of the surface intermetallic phases, the volta potentials measurements and the study of the influence of the conversion treatments on the surface volta potentials were carried out by means of SEM/EDS and AFM operating in the Kelvin Probe mode (SKPFM). This was only done for AA7075-T6 specimens both bare and coated with process 2, since this was the process which led to best results in terms of corrosion resistance.

Figure 7 shows the study performed on the bare AA7075-T6 alloy: a SEM micrograph with the EDS spectra of the two intermetallic phases, IM1 (Al-Fe-Cu with high Cu content) and IM2 (Al-Fe-Cu with low Cu content) (Figures 7a, 7b and 7c); the respective volta potential map (Figure 7d); and a volta potential section analysis performed along the intermetallics phases (Figure 7e). Figure 7 includes also the values of the maximum potential difference between the aluminum matrix and the intermetallics. The values of the volta potential obtained were representative of the general behavior of the Cu containing intermetallics. The lower the potential of the intermetallics the more cathodic they are with respect to the aluminum matrix and act as preferential sites for corrosion. Indeed, this volta potential difference between the matrix and the intermetallic is the driving force for the initiation of the corrosive phenomena.

Figure 8 shows the same information as Figure 7 but for the AA7075-T6 alloy coated with process 2. The EDS analysis on a Cu-rich intermetallic covered by local deposits/oxides due to the conversion treatment showed higher quantity of deposits/oxides in the middle of the intermetallic than in the periphery (the area adjacent to it) (Figures 8a, 8b and 8c). This difference in composition is also indicated in the volta potential map (Figure 8d) by a color variation between the middle and the periphery and in the section analysis by a potential

difference (Figure 8e). Taking into account that this measurement corresponded to a Cu-rich intermetallic, the most remarkable result was the reduction in the volta potential difference between the intermetallic and the aluminum matrix after the conversion treatment, compared to the bare AA7075-T6 alloy (Figure 7). This clearly indicated a reduction in the corrosion susceptibility of the alloy when process 2 was applied.

4. Conclusions

Novel Cr-free conversion coatings based on inorganic metallic salts (Ti/Zr/Mn/Mo) were developed at a pilot scale for the corrosion protection of the AA2024-T3 and AA7075-T6 aluminum alloys for aircraft applications.

All the coatings improved the corrosion resistance of both aluminum alloys, even in the case of the coated AA2024-T3 panels, which showed a lower corrosion performance than the coated AA7075-T6 panels. The best corrosion resistance for both alloys was achieved with the conversion process comprising formulations with Zr, Mo and Mn but not Ti salts.

The deeper study performed on the alloy AA7075-T6 revealed that oxides, hydroxides and/or fluorides of the metallic elements in the chemical conversion bath preferentially deposited on the surface of the Cu-rich intermetallics. These deposits led to a reduction of the electrochemical potential difference between the intermetallic and the aluminum matrix and provided significant corrosion protection. The protection mechanism mainly occurred with those formulations free from titanium salts; indeed, the presence of Ti compounds in the conversion bath led to detrimental salt deposits on the surface of the treated alloys.

Therefore, the titanium-free formulations containing zirconium, molybdenum and manganese from an acid or both an acid and a salt resulted in the formation of the previously described protective deposits on the Cu-rich intermetallics. The chemical composition of these deposits included Zr, Mn and Mo oxides, hydroxides and/or fluorides.

In summary, although the Cr-free conversion coatings developed in this study for the AA7075-T6 and AA2024-T3 alloys do not still meet the stringent requirements of the aircraft industry, they significantly improved the corrosion performance with respect to the bare alloys. The novel coatings could be considered as a good starting point for the aircraft application and further studies could be carried out for the coatings optimization. On the other hand, the corrosion protection provided by the current Cr-free conversion coatings based on inorganic metallic salts (Ti/Zr/Mn/Mo) might provide sufficient corrosion protection for other industrial applications.

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Table I

Percentage weight composition of selected aluminum alloys: AA 2024-T3 and AA 7075-T6
(Source: ASM International Handbook).

Alloys	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
AA2024	0.50	0.50	3.80-4.90	0.30-0.90	1.20-1.80	0.10	0.25	0.15
AA7075	0.40	0.50	1.20-2.00	0.30	2.10-2.90	0.18-0.28	5.10-6.10	0.20

Table II

Description of chromium-free conversion processes.

Process reference	Temperature (°C)	Time (min)	pH	[K ₂ TiO ₆] (g/l)	[K ₂ ZrF ₆] (g/l)	[Na ₂ MoO ₄] (g/l)	[KMnO ₄] (g/l)
1	20	3	5	4	6	20	20
2	20	3	5	0	8	20	20
3	20	3	5	0	0	20	20
4	20	3	5	8	0	20	20

Table III

Mathematical models for AA2024-T3 and AA7075-T6 alloys.

AA2024-T3	
Surface corrosion = 11.69 – 0.14 x Temperature x pH + 0.08 x [Ti] x [Mn] + 0.00581444 x Temperature ² + 0.085 x pH ² – 0.17 x [Ti] ² – 0.009 x [Mn] ²	<u>R² = 56.24%</u>
AA7075-T6	
Number of Pits = 3281.85 + 1637.2 x pH – 570.09 x [Mn] + 111.02 x Time x [Mn] – 87.33 x [Ti] x [Zr] – 96.57 x pH x [Mo] + 21.56 x [Zr]x [Mn] – 280.81 x Time ² + 50.05 x [Ti] ² + 9.83 x [Mo] ²	<u>R² = 83.58%</u>

Table IV

Tafel analysis of the polarization curves for the AA7075-T6 alloy and the AA2024-T3 alloy

Reference	E corr (V vs Ag/AgCl)	Epit (V vs Ag/AgCl)	Epit -Ecorr (V)	jcorr (A/cm ²)	βa (mV/Dec.)	βc (mV/Dec.)	Rp (.cm ²)	Efficiency (%)
2024 bare	-0,197	-0,197	0,00E+00	1,74E-06	7,5	22	1,40E+03	NA
2024-1	-0,523	-0,227	2,96E-01	1,35E-06	184	173	2,87E+04	22,41
2024-2	-0,440	-0,224	2,16E-01	5,55E-07	161	159	6,26E+04	68,10
2024-3	-0,430	-0,097	3,33E-01	1,59E-06	216	161	2,52E+04	8,62
2024-4	-0,769	-0,252	5,17E-01	9,29E-07	327	208	5,94E+04	46,61
7075 bare	-0,436	-0,436	0,00E+00	1,33E-06	5,6	360	1,80E+03	NA
7075-1	-0,565	-0,152	4,13E-01	1,54E-07	164	115	1,91E+05	88,42
7075-2	-0,625	-0,128	4,97E-01	1,34E-07	112	131	1,96E+05	89,92
7075-3	-0,694	-0,104	5,90E-01	3,25E-07	284	133	1,21E+05	75,56
7075-4	-0,666	-0,329	3,37E-01	1,97E-07	150	128	1,52E+05	85,19

Table V

Semiquantitative EDS analysis on intermetallic particles of AA7075-T6 panels treated with different processes. Results in weight%

Reference	O	F	Al	K	Ti	Mn	Cu	Zr	Mo	Total
Process 1	14,16	7,72	13,30	5,85	0,96	2,96	41,06	5,08	8,91	100
Process 2	15,06	---	36,18	2,77	---	7,16	10,95	15,59	12,28	100
Process 3	13,87	---	29,71	2,78	---	11,74	14,17	14,46	13,27	100
Process 4	13,79	---	28,98	2,77	0,74	8,49	31,56	---	13,66	100

Figure captions

Figure 1. Coatings deposited on to the AA2024-T3 alloy after 168 h of exposure in the salt spray fog corrosion test. a) Process 1; b) Process 2; c) Process 3; d) Process 4; e) Chromate conversion coating (Alodine 1200S); f) Bare (non-coated) alloy.

Figure 2. Coatings deposited onto the AA7075-T6 alloy after 168 h of exposure in salt spray fog corrosion test. a) Process 1; b) Process 2; c) Process 3; d) Process 4; e) Chromate conversion coating (Alodine 1200S); f) Bare (non-coated) alloy.

Figure 3. Potentiodynamic sweeps. a) Polarization curves performed on the AA2024-T3 alloy, b) Polarization curves performed on the AA7075-T6 alloy.

Figure 4. Tafel analysis of the polarization curves for the AA7075-T6 alloy and the AA2024-T3 alloy. a) Epit-Ecorr, b) jcorr c) Corrosion efficiency, d) Rp.

Figure 5. Surface's morphology and composition of AA7075-T6 alloy panels tested by potentiodynamic sweeps. a) SEM Untreated; b) SEM Process 2; c) SEM Process 2 (pit initiation); d) EDS Process 2.

Figure 6. SEM images of the AA7075-T6 alloy subjected to conversion processes 1 and 4 prior to SST. a) Process 2. General surface; b) Process 4. General surface; c) Process 2. Spherical deposit; d) Process 4. Spherical deposit; e) Process 2. Intermetallic particle; f) Process 4. Intermetallic particle.

Figure 7. Volta potential study for the bare AA7075-T6 alloy. a) SEM micrograph; b) EDS spectrum, IM1= Al-Fe-Cu (high Cu); c) EDS spectrum, IM2= Al-Fe-Cu (low Cu); d) Volta potential map; e) Volta potential section analysis.

Figure 8. Volta potential study for the AA7075-T6 alloy coated with Process 2. a) SEM micrograph; b) EDS spectrum, Z2 (Deposit on the intermetallic); c) EDS spectrum, Z1 (Periphery of the intermetallic); d) Volta potential map; e) Volta potential section analysis.

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