Poster ☐ Oral ☐
A decisão final será do Comitê Técnico.

Influence of pH and concentration on zirconium-based coating on T6-7075 aluminum alloy

Germano C. Rosa[a], Jéssica Salles Pinheiro [b], Jane Zoppas Ferreira[c]

New Abstract

Zirconium-based conversion coatings have been studied as a great alternative to the processes that make use of hexavalent chromium or phosphates, presenting good adhesion, uniformity, considerable corrosion resistance and are more friendly to the environment. Aluminum 7075 samples were immersed in two commercial solutions, ZR16* and ZR14*, for 240 s in two different concentrations and two different pH, 3.0 and 4.0, for each solution, in order to analyze the influence of additives, concentration and pH on the deposition. OCP measurements performed after the deposition time show about 200 mV difference between the two pH conditions of the ZR16 and 350 mV solution comparing the two conditions of greater concentration between ZR16 and ZR14. Scanning electronic microscope images showed that under conditions of higher concentration and high pH, cracks were found in the conversion coating, weakening its resistance to corrosion. The presence of additives in the ZR16 provided more uniform layers and absence of cracks.
*Klintex®

Keywords: corrosion, conversion coating, Zirconium-based Coating.

* * *

[a] Metallurgical Engineer - LACOR/PPGE3M/UFRGS
[b] MSc, Materials Engineer - LACOR/PPGE3M/UFRGS
[c] PhD. Bel in Chemistry - LACOR/PPGE3M/UFRGS

Introduction

Widely used in the aerospace industry, aluminum stands out for delivering lightness, workability with high mechanical resistance and corrosion. Every project aimed at aircraft construction uses aluminum, to a greater or lesser extent, in different alloys and applications. The AA 7075 alloy is widely used to build the wings and roof of the aircraft, as it presents the ideal characteristics for the crucial safety and performance in flight. At work, aircraft face the most diverse environmental conditions, being able to withstand temperature variations in flight ranging from -60 ° C to + 60 ° C, humid as well as extremely dry conditions. In this way, a series of treatments for their protection and prevention against degradation are necessary, especially those that view their protection against corrosion, such as prime coating, top coating, anodizing and conversion coating [1][2]. The conversion coating procedure consists of immersing the component to be coated in a chemical bath, with adjusted pH and temperature, so that the material substrate reacts with the chemical species of the bath, forming a layer of chemical compounds under the surface of the component [3]. The frequently used aluminum conversion baths contain chromium, particularly dichromate, hat offers excellent resistance to corrosion. However, currently research shows that chromium (VI) specimens have high toxicity and cancer-causing factors, thus, many European countries have already restricted their uses[4]. Hexafluorozirconium acid, used as an alternative to form zirconium-based coatings, becomes an increasingly frequent option, with results of corrosion resistance very similar to baths containing chromates, especially Cr(III). This work will focus on the analysis of pH, composition and concentration influence of zirconium (Zr) conversion baths to increase the corrosion resistance, as well as the preferred deposition sites and structural aspects of the layer deposited on the AA7075 aluminum alloy.

Materials and methods

Samples of 7075-T6 aluminum sheet of 9 cm^2 section were sanded to 1200 mesh sandpaper size, SaloClean® degreasing solution was taken for 10 minutes at 60 ° C. After being whashed with distilled water and dried, the samples were immersed in the Zr-based conversion bath for 240 s at room temperature (25 ° C). Two different commercial solutions were used for the conversion baths (ZR14 * and ZR16 *), each with its composition and with different elements in its composition. The mainly difference between the solutions is a large presence of Mo in Zr16* solution.

From the tests and previous data, two dilution concentrations were chosen for each solution, being 3.5% and 7% for ZR14 * and 2.5% and 2.9% for ZR16 *, aiming to evaluate the action of concentration on deposition and film thickness. The pH ranges chosen were 3.0 and 4.0 in order to analyze the influence of pH on the deposition reaction. OCP analyzes were performed during the conversion coating to determine the reaction behavior for each pH range and solution concentration. Images via scanning electron microscope (SEM) were obtained to verify the surface of the samples, determine preferential deposition sites, uniformity of the deposited layer and its integrity. Dispersive energy spectroscopy (EDS) measurements were used to determine point composition on the surface in order to verify the effective deposition at several points, as well as whether there are preferred deposition sites.

Results and discussion

The immersion time during the conversion coating must be one of the variables to be controlled because the film thickness is also strongly linked to the treatment time [5]. After reaching the surface activation energy, the deposition begins in priority cathodic zones, formed mainly by the intermetallic precipitates and the substrate/intermetallic interface [6]. After this initial instant, the system tends to find its stability and the deposition kinetics tends to increase the thickness of the film from the deposited cores [7]. Due to the fragility of this nanometric film and its high internal tension, with significantly increase in the thickness of oxide, cracks can occur creating narrow unprotected sites and possibly fragile to corrosion. In addition to impairing the application of subsequent processes such as top coating. The time of 240 s of immersion was fixed because, as it can be seen in Figure 1, under all conditions the OCP was stabilized in this step. This is important since the time is decisive to create a film of zirconium oxide as an uniform surface, with a thickness that is effective to improve corrosion resistance. Samples with ZR16 bath application, for both concentrations, the pH more acid undergo a small surface activation during the first 100 s, due to the dissolution of the surface oxide present in the aluminum until they find stability at about - 0.95 V vs. Ag/AgCl close to 240s [8][9]. Meanwhile, the samples in the same bath with a more alkaline pH demonstrate a shorter surface activation time, around 75 s and reach values close to stability more quickly. This indicates that the higher pH associated to the molybdenum, present in the ZR16 conversion solution, influences the lower need for surface activation in order to form the conversion coating layer [10].

The ZR14 solutions have more negative potential values compared to ZR16. For concentrations of 7%, the more alkaline pH (pH 4.0) presents potential values of –1.2 V vs. Ag/AgCl, while with pH 3.0, stability is achieved at –1.5V vs. Ag/AgCl. For a lower concentration of 3.5% and pH 4.0, the surface activation time is 175 s, showing a tendency for more time spent to dissolve oxide and less deposition nuclei were formed, thus also growth of the film thickness, stability is reached around –1.15V vs. Ag/AgCl in 240 s[11]. The same phenomenon is not present for a more acidic pH, the activation of the substrate is carried out in 100 s and stability is reached in 200 s, the pH decrease indicates shorter surface activation time and more time for the conversion coating to grow.

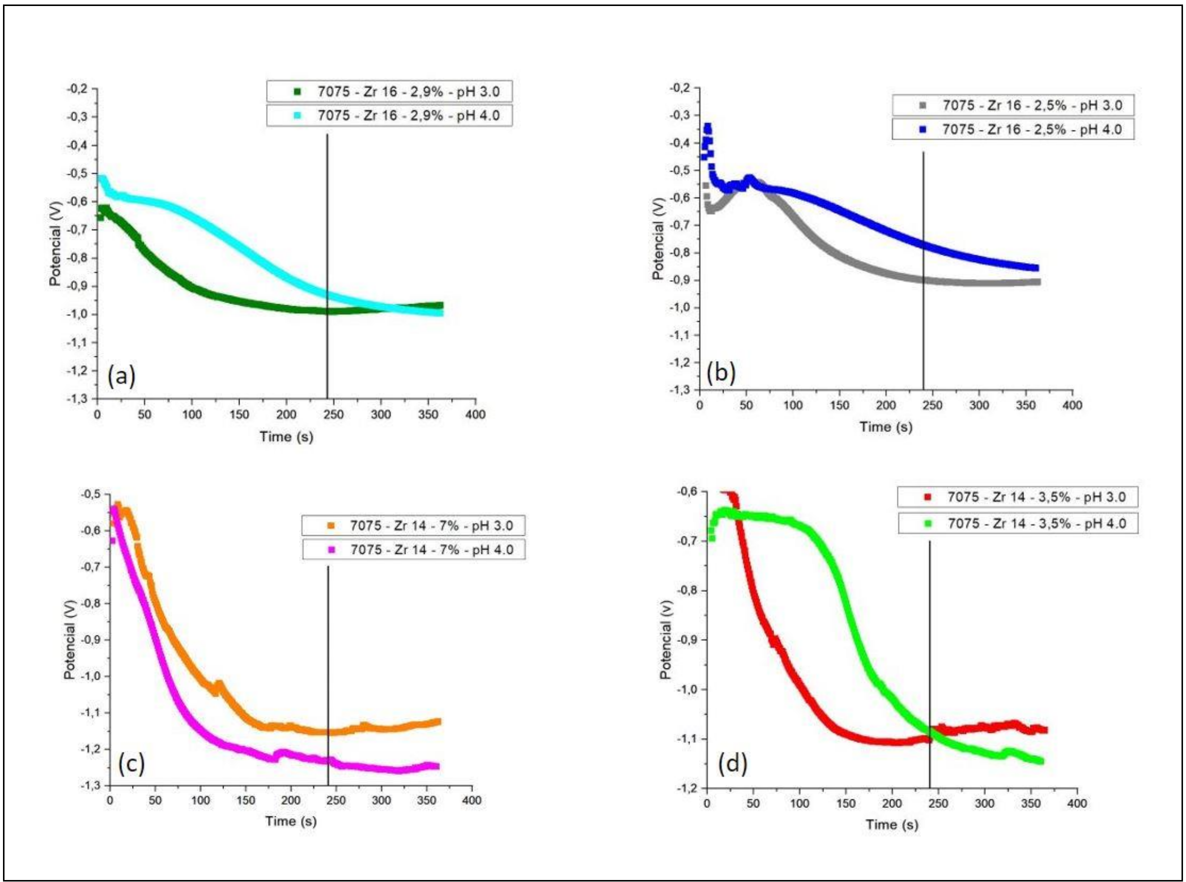

Figure 1 – OCP measurements (a) ZR16 – 2,9%, (b) ZR16 – 2,5%, (c) ZR14 – 7% and (d) ZR14 – 3,5%.

Reactions that command deposition of the conversion coating are strongly linked to pH [12]. When these coatings are discussed exclusively Zr-based treatments, ranges of pH from 2.0 to 4.0, can thicken too much the film, when coupled to variation of Zr concentrations and additives in the solution formulation bring different deposition results, as we can see in Figure 2.

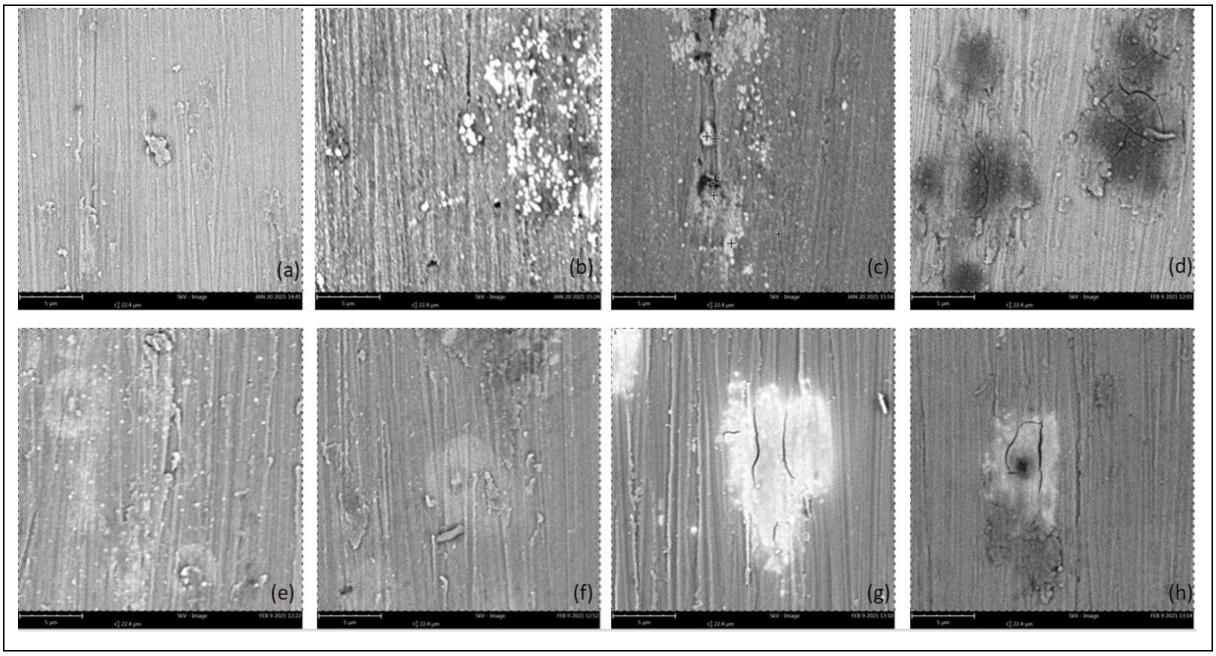

Figure 2 – SEM images (a) ZR14 – 7% - pH 4, (b) ZR16 – 2.9% - pH 4, (c) ZR16-2.9%-pH 3, (d) ZR14-3.5%-pH 3, (e) ZR16-2.5%-pH 4, (f) ZR16-2.5%-pH 3, (g) ZR14-3.5%-pH 4 e (h) ZR14-7%-pH 3.

Conditions with a more alkaline pH proved to be more effective in terms of depositing zirconium more evenly on the surface when combined with additives such as Mo, present in the ZR16 solution. Zr and its agglomerates preferably precipitated around intermetallic particles present in the aluminum matrix of AA7075-T6 [6]. The high presence of precipitates and white area in Figure 2 (e) (b), shows a large amount of Zr, identified in Table 1. It is also possible to note the presence of Mo.

Table 1 – Samples covered analyzed by energy dispersive x-ray (EDS)

Conditions	Elements (Weight Conc.)							
	Al	O	Zr	Zn	F	Fe	Mn	Mo
ZR14-7%-pH 4	65.21	10.42	11.78	7.9	2.17	0.51	2.01	-
ZR16-2.9%-pH 4	36.75	21.46	22.68	1.78	-	-	2.67	14.66
ZR16-2.9%-pH 3	66.48	11.58	5.27	6.38	0.17	1.16	-	8.96
ZR14-3.5%-pH 3	64.44	13.05	13.6	6.56	1.11	1.24	-	-
ZR16-2.5%-pH 4	40.6	24.68	26.6	3.93	-	-	-	4.19
ZR16-2.5%-pH 3	63.87	12.12	10.86	6.26	-	-	-	6.89
ZR14-3.5%-pH 4	45.62	19.09	26.75	6.14	1.62	-	0.78	-
ZR14-7%-pH 3	67.34	13.89	12.76	5.58	0.43	-	-	-

When the samples treated with coating solution ZR14 are observed, as in Figure 2 (a, d, g, h), large dense whitish areas can be noticed, rich in Zr. However, there is low uniformity in deposition throughout the samples and the great film thickness provides cracks in the coating, probably as a result of internal stressing thick films while the layer dried [13][14]. The long surface activation time verified by OCP during deposition indicates that there was a greater action in certain nuclei, thus, the coating became irregular and fragile. Since a lower concentration of Zr was detected by EDS, the coating appears to have deposited only in a few places, which indicates lack of uniformity. The lower pH presents less efficiency in deposition even on the preferred places compared to the same condition in a more alkaline pH.

Conclusion

The pH 4.0 was more effective for the deposition of zirconium coating for the most conditions studied; the more alkaline pH favors the reaction with the aluminum substrate, forming more dense films and covering the surface. That translates to higher values of OCP, that is, better protection of the surface from the effects of corrosion.

Intermetallic presence on the surface of the material, forming cathodic zones, favors the deposition of zirconium on these sites, so that the reaction begins in these areas and grows to the rest of the surface. In cases where the pH solution is lower, there is greater activation of the surface, the film deposits significantly in these places, weakening and cracking its structure.

The use of Mo as an additive allows the zirconium deposition in several places over the surface and creates optimum thickness without breaking the oxide film. Combining a low concentration of zirconium and more alkaline pH, an optimum condition that provides good corrosion resistance is achieved for the application of subsequent top coating.

References

[1] T. G. Harvey,Corros. Eng. Sci. Technol.,48, 248 (2013).

[2] M. Forsyth, M. Seter, M. Y. Tan, and B. Hinton,Corros. Eng. Sci. Technol.,49, 130(2014).

[3] I. Milosev , G. S. Frankel. Journal of The Electrochemical Society,165(3) C127-C144 (2018).

[4] https://ec.europa.eu/commission/presscorner/detail/en/IP_10_1465 (2010).

[5] J. Winiarski, J. Masalski, and B. Szczygieł,Surf. Coat. Technol.,236, 252 (2013).

[6] P. Santa Coloma, U. Izagirre, Y. Belaustegi, J. B. Jorcin, F. J. Cano, and N. Lapena,Appl. Surf. Sci.,345, 24 (2015).

[7] N. W. Khun, G. S. Frankel, and J. Zimmerman,Corrosion,69, 259 (2013).

[8] I. Schoukens, I. Vandendael, J. De Strycker, A. A. Saleh, H. Terryn, andI. De Graeve,Surf. Coat. Technol.,235, 628 (2013).

[9] F. Andreatta, A. Turco, I. de Graeve, H. Terryn, J. H. W de Wit, and L. Fedrizzi,Surf. Coat. Technol.,201, 7668 (2007).

[10] H. Eivaz Mohammadloo and A. A. Sarabi,Appl. Surf. Sci.,387, 252 (2016)

[11]L. Li, A. L. Desouza, and G. M. Swain,Analyst,138, 4398 (2013).

[12]L. Li, B. W. Whitman, and G. M. Swain,J. Electrochem. Soc.,162, C279(2015).

[13] T. Lostak, S. Krebs, A. Maljusch, T. Gothe, M. Giza, M. Kimpel, J. Flock, andS. Schulz,Electrochimica Acta,112, 14 (2013).

[14] A. Yi, J. Du, J. Wang, S. Mu, G. Zhang, and W. Li,Surf. Coat. Technol.,276,239(2015)