

# Characterization of corrosion resistance of chromium-free conversion coatings for aeronautical application

L. Belsanti, E. Forchin, R. Stifanese, M. Toselli, P. Traverso

*Coating systems protect metal substrates from environmental corrosion attack. However, although having good performances, the presence of specific metal ions in their composition represents a potential source of environmental contamination. The necessity to conciliate corrosion protection with environmental impact is, thereby, primary.*

*This work was designed to study the performance of low environmental impact conversion coatings (surface pre-treatment and high-solids epoxy primer), such as those free from hexavalent chromium (Cr VI), layered on different substrates of aluminium alloy [Al 7075 (T6) unclad and Al 2024 (T3) unclad] widely used in aerospace applications. Substrate surfaces were first treated by environmentally friendly Cr-free products. Successively, on pre-treated substrates, high-solids, chromate-free epoxy primer was applied. The capability to protect substrates from corrosion phenomena was evaluated following exposure of 4 groups of samples to in situ marine atmosphere at the Genoa Experimental Marine Station (G.E.M.S.) of C.N.R.-I.S.MAR., located in the port of Genoa, for 8, 16, and 24 months and in accordance with UNI EN ISO 8565:1997 Standard. Accelerated degradation of conversion coating was also studied by electrochemical impedance spectroscopy. To characterize the coating systems, the interface metal substrate/conversion coating, sections from different samples were submitted to microscope techniques. The experimental results reported in this paper give useful information regarding the protective power against substrate corrosion of some Cr-free conversion coatings that have, as compared to traditional Cr VI containing products, a lower impact on workers' health and on the environment.*

**KEYWORDS:** AL ALLOYS - CONVERSION COATING - CORROSION PROTECTION

## Lucrezia Belsanti

*Institute for Environmental Protection and Research (I.S.P.R.A.),  
Via Vitaliano Brancati 48, 00144 Rome, Italy -  
National Research Council (C.N.R.) -  
Institute of Marine Sciences (I.S.MAR.)  
Genoa Dept., Via A. De Marini 6, 16149 Genoa, Italy*

## Emiliano Forchin

*Agusta Westland, Via G. Agusta 520,  
21017 Cascina Costa di Samarate (VA), Italy*

## Roberto Stifanese, Milena Toselli, Pierluigi Traverso

*National Research Council (C.N.R.)  
Institute of Marine Sciences (I.S.MAR.) Genoa Dept.,  
Via A. De Marini 6, 16149 Genoa, Italy  
(corresponding author  
Pierluigi Traverso pierluigi.traverso@ismar.cnr.it)*

## INTRODUCTION

The high strength Al alloy 7075 and Al alloy 2024 have been usually utilized in aerospace applications [1]. These alloys are subject to a high degradation in chloride ion environments and it is necessary to improve their corrosion resistance and adhesion properties. For this reason, the development of various surface modification processes have been studied [2].

Among them, conversion coatings play a key role because they protect metallic substrates against environmental corrosion attack and favour the adhesion of further top coat applications [3-10]. However, although having good performances, the presence of specific metal ions in their composition such as hexavalent chromium (Cr VI) represents a potential source of environmental contamination and a risk factor for workers' health [11-14]. The necessity to conciliate corrosion protection with environmental impact is, thereby, primary [15-24], and the development of a chromate-free conversion coating with equal or better performances becomes of great importance [25,26]. To this aim, trivalent chrome processes, rare earth based conversion coatings, permanganate and Zr/Ti based treatments have been

studied but their long term corrosion resistance has been often found to be inadequate in aggressive chloride containing environments [27-29].

The main objective of this work was to study the performance of two low environmental impact conversion coatings (surface treatment and primer) free from Cr VI, layered on Al alloy 7075 and Al alloy 2024.

The protection of these Al alloys against corrosion phenomena was studied by exposing 4 groups of samples to marine atmosphere at the Genoa Experimental Marine Station (G.E.M.S.) of C.N.R.-I.S.MAR., located in the port of Genoa, for 8, 16, and 24 months and in accordance with UNI EN ISO 8565:1997 Standard. The G.E.M.S. of C.N.R.-I.S.MAR. is frequently used for the conduction of corrosion tests on materials and for the assessment of anticorrosive and antifouling power of different types of coating. To these aims, samples can be directly immersed in sea water (from a floating dock) or exposed to marine atmosphere (by appropriate structures) [http://www.ismar.cnr.it].

The effective capability of low environmental impact conversion

coatings to protect substrates from corrosion was evaluated at the end of each time of exposure to marine atmosphere. At the same time, the possible presence of aesthetic damages was evaluated. To this aim samples were analyzed by picture collection by digital camera, optical and electron microscope, and electrochemical tests.

Our results give useful information in choosing reduced environmental impact products having, at the same time, high quality and protection levels.

## MATERIALS AND METHODS

### Materials

#### *Substrates and Cr-free conversion coatings*

Two aluminium alloys were utilized as substrates: Al alloy 7075 (T6) unclad and Al alloy 2024 (T3) unclad. Substrate surfaces were pre-treated in two ways, and the same epoxy primer was successively applied. Samples were then divided in 4 groups as specified in Table 1.

**Tab. 1** - Conversion coatings under investigation and their grouping (\*)

Group	Substrate	Surface pre-treatment and primer	Thickness ( $\mu\text{m}$ )
1	Al alloy 7075 (T6) unclad	Water based adhesion promoter and Cr-free high-solids epoxy primer	$34 \pm 3$
2	Al alloy 7075 (T6) unclad	Sol-gel pre-treatment with Cr-free corrosion inhibitor and Cr-free high-solids epoxy primer	$37 \pm 3$
3	Al alloy 2024 (T3) unclad	Water based adhesion promoter and Cr-free high-solids epoxy primer	$38 \pm 2$
4	Al alloy 2024 (T3) unclad	Sol-gel pre-treatment with Cr-free corrosion inhibitor and Cr-free high-solids epoxy primer	$30 \pm 3$

(\*) = due to confidentiality requirements, it is not possible to provide additional information.

Samples were 7,5 cm x 7,5 cm. Before exposure to marine atmosphere, artificial defects were created on some samples to amplify conversion coatings damage. In accordance with the International Standard Guidelines, defects were represented by two diagonal scratches deep enough to reach the aluminium substrate, 5 cm long and orthogonal one each other. Samples were analyzed with or without defects (scratched and unscratched samples).

### Methods

#### *Photographic documentation*

Qualitative and preliminary evaluation of the decay or integrity of conversion coatings after exposure to marine atmosphere was given by a detailed, although macroscopic, photographic documentation of the morphology of specimens by using a high performance digital camera (Canon EOS 500D with a Canon lens 50 mm f 1.7) recording pictures at 12.2 MP resolution in RAW format.

#### *Thickness measurement*

Conversion coating thickness was evaluated as applicable according to Eddy Current method (Namicon DuoCheck ST1) by the suitable probe for not-magnetic substrates. Assessments were performed on five different points for each sample, before exposure to marine atmosphere.

The values are reported in Table 1 as the mean  $\pm$  S.D. for each group of samples.

#### *Microscope analysis*

Following 0, 8, 16, and 24 months of exposure to marine atmosphere, samples were submitted to two steps in-depth analyses performed by using Optical Stereo Microscope (Wild M3B) with 3D micrograph acquisition system and by Scanning Electron Microscope (Leo 1450VP) with EDX microprobe (Oxford Inca 300) respectively. SEM was set up at 20 kV acceleration voltage.

#### *Electrochemical impedance spectroscopy measurement*

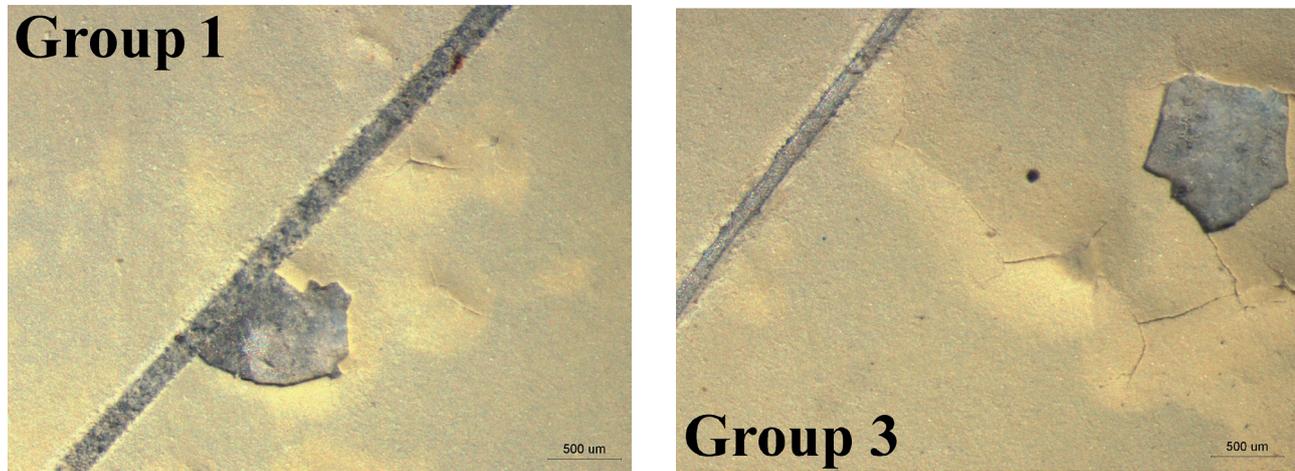
Following 0, 8, 16, and 24 months of exposure to marine atmosphere, unscratched samples were analysed after exposure to 5% NaCl aqueous solution (corrosive solution), at room temperature, for 2, 24, 48 (only for samples exposed to marine atmosphere), 72, and 168 hours (7 days). Electrochemical impedance spectroscopy (EIS) measurements were carried out by using an electrochemical device (Metrohm Autolab PGSTAT 30) interfaced with a pc having a suitable software (Metrohm FRA). All EIS measurements were performed by perturbing the equilibrium potential of the specimen with 10 mV ac with the frequency decreasing from 10 KHz to 10 mHz. The impedance values were plotted in Nyquist diagrams. From Bode diagrams, values of Z modulus ( $|Z|$ , expressed in  $\Omega \text{ cm}^2$ ) were also calculated.

These values represent a first indication of the protective power of the coating system.

## RESULTS AND DISCUSSION

OM and SEM analyses following exposure to marine atmosphere

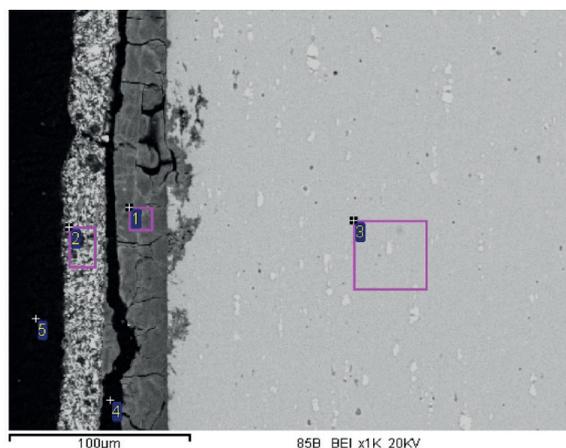
All samples belonging to the four eco-friendly groups of protective systems were submitted to OM and SEM analyses. However, for conciseness reasons, only one representative picture collected by OM and SEM from one sample is shown.



**Fig. 1** - Stereomicroographies of group 1 and 3 conversion coating appearance after 24 months of exposure to marine atmosphere.

Figure 1 shows two scratched samples representing groups 1 and 3 characterized by the same surface pre-treatment and primer but differing for the substrate. Following 24 months of exposure to marine atmosphere, both samples show similar high blistering and cracking degradation of the conversion coating.

SEM measurements on samples from group 1 could reveal the presence of possible corrosion damages responsible for cracking and the subsequent detachment of the conversion coating found to occur following 24 months of exposure to marine atmosphere.

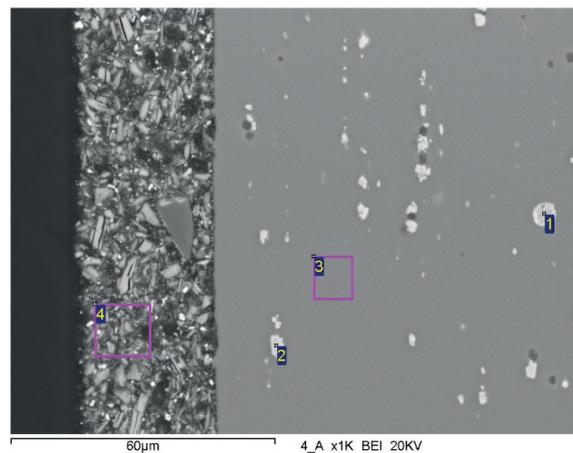


Spectrum	In stats.	O	Mg	Al	P	S	Ca	Ti	Cu	Zn	Ba	Total
1	Yes	61.83	1.17	27.65	0.93	2.12				6.29		100.00
2	Yes	41.99		0.78	10.98	1.70	0.88	7.69		30.15	5.84	100.00
3	Yes	1.57	2.59	88.41					1.65	5.78		100.00

**Fig. 2** - SEM analysis of group 1 conversion coating after 24 months of exposure to marine atmosphere. Morphology (upper panel) and chemical analysis (lower table). Values are reported in weight %.

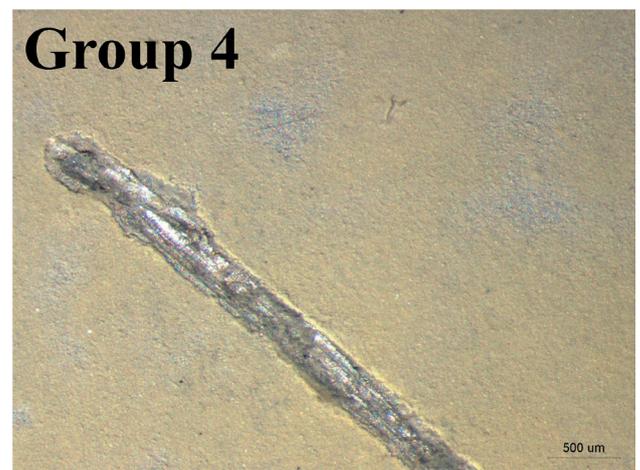
As shown in Figure 2, SEM analysis identifies the presence of fissures in the interface metal substrate/conversion coating as compared to not exposed samples (Figure 3, area n. 4). Chemical analysis shows the presence of very high amount of oxygen (Figure 2, area n. 1) due to the formation of corrosion products

of the substrate, leading to a detach between conversion coating and substrate. Similar data were also obtained from group 3. For shorter times of exposure to marine atmosphere (8 and 16 months), blistering and cracking of conversion coatings for samples from group 1 and 3 were very poorly detectable.



Spectrum	In stats.	O	Mg	Al	P	Ca	Ti	Fe	Cu	Zn	Ba	Total
1	Yes		11.86	49.29					20.61	18.24		100.00
2	Yes			57.38				12.62	30.00			100.00
3	Yes		3.06	89.68					1.13	6.12		100.00
4	Yes	42.25			10.75	1.98	8.50	0.69		29.12	6.72	100.00

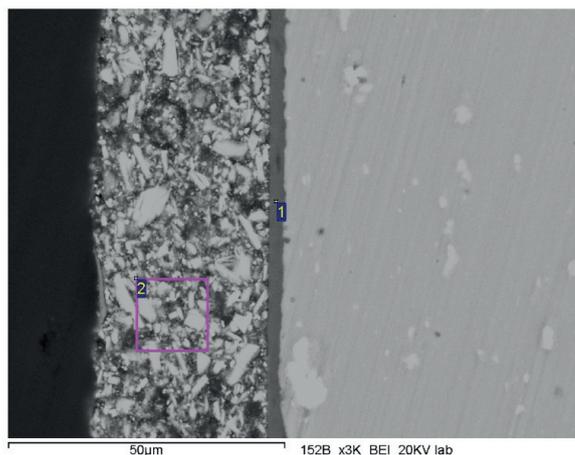
**Fig. 3** - SEM analysis of group 1 conversion coating before exposure to marine atmosphere. Morphology (upper panel) and chemical analysis (lower table). Values are reported in weight %.



**Fig. 4** - Stereomicrographies of group 2 and 4 conversion coating appearance after 24 months of exposure to marine atmosphere.

Figure 4 shows two scratched samples belonging to groups 2 and 4 characterized by the same surface pre-treatment and primer but differing for the substrate. Following 24 months of exposure to marine atmosphere, in contrast to what observed on samples from groups 1 and 3, both samples representing groups 2 and 4 do not show significant blistering or cracking degradation of the conversion coating.

SEM measurements on samples from group 2 reveal that, following 24 months of exposure and in contrast to what observed to occur on samples from groups 1 and 3, no fissures are detectable and that the conversion coating is still homogeneously distributed. This is further confirmed by the picture shown in Figure 5.

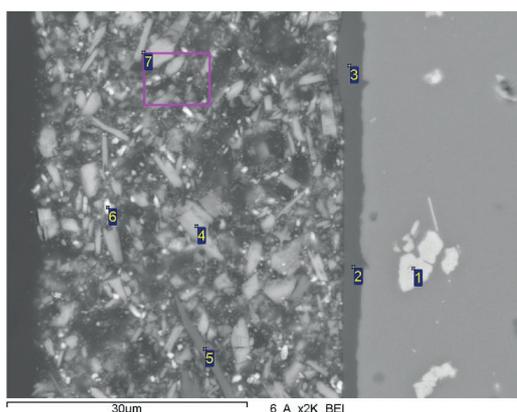


Spectrum	In stats.	O	Al	Si	P	S	Ca	Ti	Zn	Zr	Total
1	Yes	44.54	17.09	19.57					1.25	17.55	100.00
2	Yes	43.87	1.20		11.07	1.78	0.82	8.33	32.93		100.00

**Fig. 5** - SEM analysis of group 2 conversion coating after 24 months of exposure to marine atmosphere. Morphology (upper panel) and chemical analysis (lower table). Values are reported in weight %.

In addition, the integrity of the entire conversion coating, that could be modified by the formation of substrate corrosion

products, appears to be unaffected (Figure 6).



Spectrum	In stats.	O	Al	Si	P	Ti	Fe	Cu	Zn	Zr	Ba	Total
1	Yes		56.87				12.32	30.81				100.00
2	Yes	45.53	15.74	19.72		0.56			1.56	16.89		100.00
3	Yes	44.19	17.49	19.78					1.55	17.00		100.00
4	Yes	43.64			15.13	0.81			40.42			100.00
5	Yes	62.51	8.53	11.41	2.89	6.85	1.04		6.77			100.00
6	Yes	40.76	1.40		6.83	19.49			20.45	11.07		100.00
7	Yes	39.94			11.78	8.43	0.83		30.90	8.12		100.00

**Fig. 6** - SEM analysis of group 2 conversion coating before exposure to marine atmosphere. Morphology (upper panel) and chemical analysis (lower table). Values are reported in weight %.

Chemical analysis reveals the presence of oxygen in relatively high amounts (Figure 5, area n. 1). However, if compared to those measured on samples from groups 1 and 3, these levels are not suggesting the presence and, thereby, the formation of substrate corrosion products. This hypothesis is further confirmed by SEM analysis performed on unexposed samples in which oxygen is found to be present in almost the same amounts (Figure 6, areas n. 2 and n. 3). The presence of oxygen could be attributed, in this case, to the aqueous nature (sol-gel) of the surface pre-treatment performed.

### EIS analyses after exposure to marine atmosphere

EIS measurements were carried out on all the unscratched samples belonging to the four eco-friendly groups herein considered. However, for conciseness reasons and because similar results were obtained from groups 3 and 4 respectively, only Nyquist diagrams of the impedance measurements performed on groups 1 and 2 are reported below.

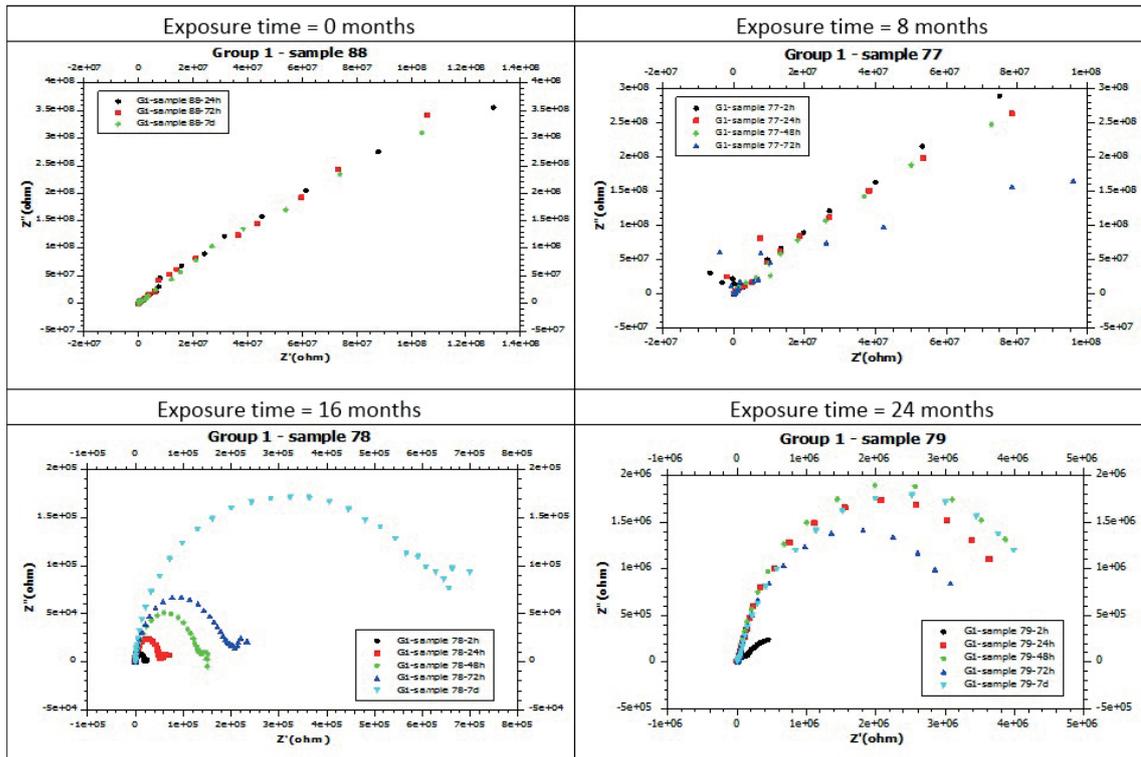


Fig. 7 - Nyquist diagram of group 1 after different immersion times in 5% NaCl solution.

As shown in Figure 7, EIS measurements on samples of group 1 unexposed to marine atmosphere show a stable trend. However, after for 7 days of immersion time in the corrosive solution, a reduction in the semicircle diameter is detectable starting from 8 months of exposure to marine environment, thereby suggesting a reduction in protective power of the conversion coating. For

longer times of exposure to marine atmosphere (16 and 24 months), semicircle diameters do not show trends related to the times of immersion in the corrosive solution. Nyquist diagrams plotted from samples of group 2 do not show trends significantly linked to the times of immersion in the corrosive solution (Figure 8).

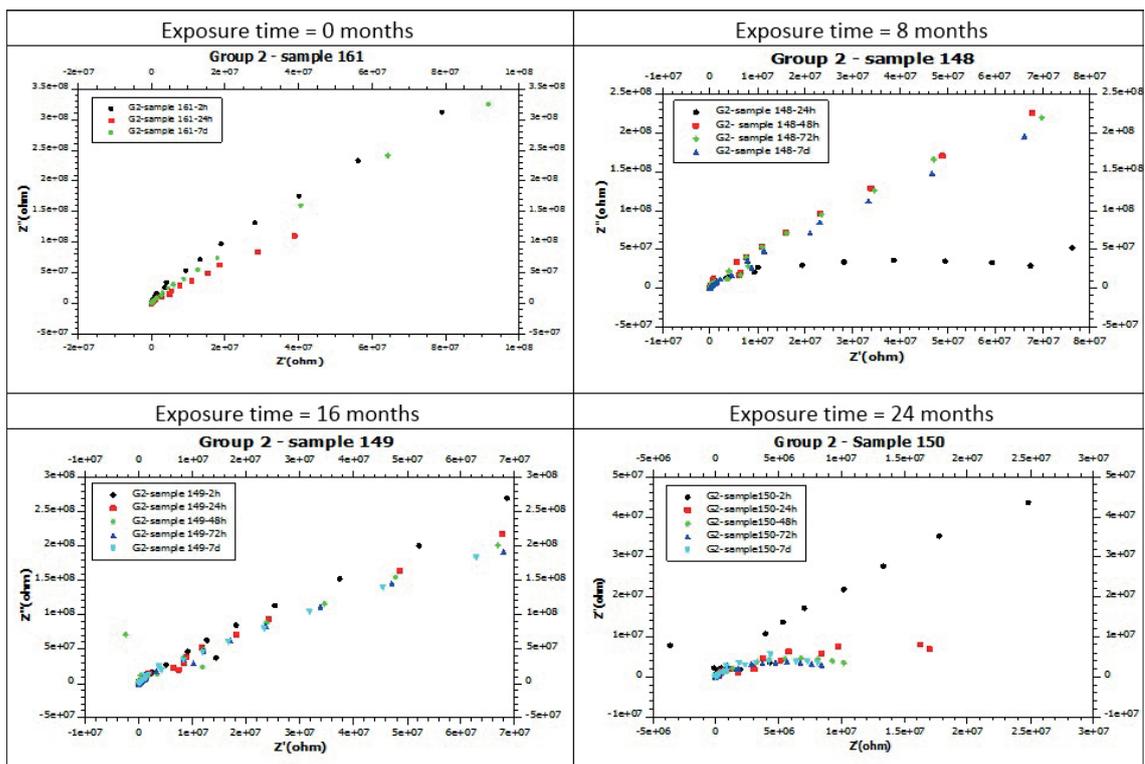


Fig. 8 - Nyquist diagram of group 2 after different immersion times in 5% NaCl solution.

Different semicircle diameters for samples after 2 hours of immersion in the corrosive solution suggests that the time of exposure to the corrosive action of the solution was not sufficient to reach the equilibrium of the electrochemical system.

To give a first indication of the degradation of the conversion

coatings, from Bode diagrams values of Z modulus ( $|Z|$ , expressed in  $\Omega \text{ cm}^2$ ) were also calculated. From the curve corresponding to  $\log |Z|$  vs.  $\log \omega$ , we have obtained the maximum asymptotic value of  $|Z|$  for lower frequencies and have considered it to be indicative of the conversion coating protective power [30].

**Tab. 2** -  $|Z|$  values following different marine atmosphere exposure times at different immersion periods in 5% NaCl solution.

Marine atmosphere exposure time = 0 months					Marine atmosphere exposure time = 8 months					
Group	$ Z _{2h}$	$ Z _{24h}$	$ Z _{72h}$	$ Z _{7d}$	Group	$ Z _{2h}$	$ Z _{24h}$	$ Z _{48h}$	$ Z _{72h}$	$ Z _{7d}$
1	-----	$3,80 \cdot 10^{+08}$	$7,59 \cdot 10^{+08}$	$3,24 \cdot 10^{+08}$	1	$3,02 \cdot 10^{+08}$	$2,75 \cdot 10^{+08}$	$2,57 \cdot 10^{+08}$	$1,91 \cdot 10^{+08}$	-----
2	$3,39 \cdot 10^{+08}$	$1,15 \cdot 10^{+08}$	-----	$3,72 \cdot 10^{+08}$	2	-----	$5,75 \cdot 10^{+08}$	$2,34 \cdot 10^{+08}$	$2,29 \cdot 10^{+08}$	$2,09 \cdot 10^{+08}$
3	$3,80 \cdot 10^{+08}$	$3,39 \cdot 10^{+08}$	$3,24 \cdot 10^{+08}$	$2,88 \cdot 10^{+08}$	3	-----	-----	-----	-----	-----
4	$5,62 \cdot 10^{+08}$	$4,68 \cdot 10^{+08}$	-----	$1,55 \cdot 10^{+08}$	4	-----	$1,38 \cdot 10^{+08}$	$1,29 \cdot 10^{+07}$	$5,62 \cdot 10^{+06}$	$2,14 \cdot 10^{+04}$

Marine atmosphere exposure time = 16 months					Marine atmosphere exposure time = 24 months						
Group	$ Z _{2h}$	$ Z _{24h}$	$ Z _{48h}$	$ Z _{72h}$	$ Z _{7d}$	Group	$ Z _{2h}$	$ Z _{24h}$	$ Z _{48h}$	$ Z _{72h}$	$ Z _{7d}$
1	$2,45 \cdot 10^{+04}$	$7,08 \cdot 10^{+04}$	$1,51 \cdot 10^{+05}$	$2,34 \cdot 10^{+05}$	$7,08 \cdot 10^{+05}$	1	$5,01 \cdot 10^{+05}$	$3,80 \cdot 10^{+06}$	$4,07 \cdot 10^{+06}$	$3,16 \cdot 10^{+06}$	$4,17 \cdot 10^{+06}$
2	$2,75 \cdot 10^{+08}$	$2,29 \cdot 10^{+08}$	$2,14 \cdot 10^{+08}$	$2,04 \cdot 10^{+08}$	$1,95 \cdot 10^{+08}$	2	$5,01 \cdot 10^{+07}$	$3,47 \cdot 10^{+07}$	$1,12 \cdot 10^{+07}$	$8,91 \cdot 10^{+06}$	$8,71 \cdot 10^{+06}$
3	$2,29 \cdot 10^{+08}$	$1,82 \cdot 10^{+08}$	$1,62 \cdot 10^{+08}$	$1,62 \cdot 10^{+08}$	$4,27 \cdot 10^{+07}$	3	$6,61 \cdot 10^{+07}$	$5,01 \cdot 10^{+05}$	$1,45 \cdot 10^{+06}$	$1,70 \cdot 10^{+06}$	$4,17 \cdot 10^{+06}$
4	$1,17 \cdot 10^{+08}$	$9,33 \cdot 10^{+07}$	$8,51 \cdot 10^{+07}$	$7,94 \cdot 10^{+07}$	$5,13 \cdot 10^{+07}$	4	$4,68 \cdot 10^{+06}$	$1,48 \cdot 10^{+06}$	$9,12 \cdot 10^{+05}$	$7,76 \cdot 10^{+05}$	$3,09 \cdot 10^{+05}$

The indicated times (2h, 24h, 48h, 72h, and 7d) refer to the immersion periods in 5% NaCl solution.

As shown in Table 2,  $|Z|$  values from samples of group 1 confirm the reduction of protective power for exposure times to marine atmosphere longer than 8 months. On the contrary, the protective power of conversion coatings for the groups 3 and 4 is reduced following times of exposure to marine atmosphere longer than 16 months.  $|Z|$  values obtained from group 2 show a high protective power that remains unchanged increasing the time of exposure to marine atmosphere.

EIS measurements show, in particular, that the group 2 has a noticeable protective power, sometimes comparable with that shown by samples whose conversion coatings are classified as non-environmentally friendly and that we have analysed in a larger study using the same experimental conditions. In this study,  $|Z|$  values obtained from Cr-containing conversion coatings reached values very next to  $10^{+9}$  that remained quite stable even increasing the time of exposure to marine atmosphere [31]. Considering the other samples (groups 1, 3, and 4), the resistance of the conversion coatings to degradation phenomena is reduced with the increase of marine atmosphere exposure time, starting from 8 months for group 1 and from 16 months from groups 3 and 4.

The results shown in this paper, further confirm the high potential of water based adhesion promoter with high-solids chromate free primer for the replacement of the chromate-based conversion coatings with environmental friendly processes, such as sol-gel methods, rare earth based treatments, etc. as reported in recent works [32-34].

## CONCLUSIONS

Two different conversion coatings applied on two aluminum alloy substrates usually utilized in aerospace applications, were studied in this work. The presence of damages and the protective power of different conversion coatings were evaluated at the end of each time of exposure to marine atmosphere.

Data acquired reveal that, if the same pre-treatment and primer are used, the aluminum alloy substrate has no influence on conversion coatings degradation, and that samples coated with sol-gel surface pre-treatment containing Cr-free corrosion inhibitor and Cr-free high-solids epoxy primer (groups 2 and 4) show a lower degradation, after 24 months of atmosphere exposure time, in comparison with the other two groups having a different conversion coating (groups 1 and 3).

This paper gives useful information in choosing reduced environmental impact products having, at the same time, high quality and protection levels. Chromium free conversion coatings could therefore replace chromate-based surface treatments, although there is still much research to be done to develop and improve a final hi-tech commercial product.

## REFERENCES

- [1] M.N. Ilman, P.T. Kusmono, Iswanto, Mater. Des., 2013, 50, 235-243.
- [2] K.A. Yasakau, J. Tedim, M.J. Zheludkevich, M.G.S. Ferreira: in "Handbook of Smart Coatings for Material Protection", Woodhead Publishing, 2014, 224-274.

- [3] B. Hinton: *Corrosion*, 2010, 66 (8), 1-15.
- [4] E. Eichinger, J. Osborne and T. Van Cleave: *Met. Finish.*, 1997, 95 (3), 36-41.
- [5] P. Yu, J.O. Stoffer, T.J. O'Keefe, X. Lin, Y. Wu and E. Morris: *Proc. Int. Waterborne, High Solids, Powder Coat. Symp.*, New Orleans, LA, USA, February 1998, The University of Southern Mississippi, Vol. 15, 409-422.
- [6] J.O. Stoffer and T.J. O'Keefe: "Environmentally compliant Coatings using non-chromated systems", S442011, AFRLMLWPTR20014163, ADA398836, Air Force Research Laboratory (AFRL), (NTIS), Springfield, VA, USA, 2001.
- [7] M.W. Kendig and R.G. Buchheit: *Corrosion*, 2003, 59 (5), 379-400.
- [8] J.H. Osborne: *Prog. Org. Coat.*, 2001, 41 (4), 280-286.
- [9] A.S. Hamdy, A.M. Beccaria and P. Traverso: *Surf. Interface Anal.*, 2002, 34 (1), 171-175.
- [10] F. Mansfeld and Y. Wang: *Br. Corros. J.*, 1994, 29 (3), 194-200.
- [11] F. Mansfeld and Y. Wang: "Corrosion protection of high-copper aluminum alloys by surface modification", *Proc. 7<sup>th</sup> Int. Symp. On "Oxide films on metals and alloys"*, Miami Beach, FL, USA, October 1994, Electrochemical Society Inc., 200-215.
- [12] F. Mansfeld, H. Shin and Y. Wang: "Method for creating a corrosion-resistant aluminium surface", US Patent 5194138, 1993.
- [13] F. Mansfeld and Y. Wang: *Mater. Sci. Eng. A*, 1995, A198 (1-2), 51-61.
- [14] J. Hu, X. Zhao, S.W. Tang and M.R. Sun: *Surf. Coat Technol.*, 2006, 201 (6), 3814-3818.
- [15] X. Lin, E. Morris, P. Yu, T.J. O'Keefe and J.O. Stoffer: "Electrochemical aspects of coating systems for the corrosion protection of aluminium", *Proc. 1<sup>st</sup> Non-Ferrous Processing and Technology Conf.*, St. Louis, MO, USA, March 1997, ASM International, 493-499.
- [16] J.O. Stoffer, T.J. O'Keefe, E. Morris, S. Hayes, P. Yu and M. Pittman: *Polym. Mater. Sci. Eng.*, 2000, 83, 311-312.
- [17] J.O. Stoffer, T.J. O'Keefe, M.J. O'Keefe, S. Hayes, E. Morris, P. Yu and X. Lin: *Int. SAMPE Tech. Conf.*, 2000, 32, 879-888.
- [18] B.R.W. Hinton: *Met. Finish.*, 1991, 89 (9), 55-61.
- [19] B.R.W. Hinton: *Met. Finish.*, 1991, 89 (10), 15-20.
- [20] M. J. Henderson, B.R.W. Hinton, A.E. Hughes, R.J. Taylor, P.N. Trathen and L. Wilson: "Chromate-free conversion coating processes", *Proc. Asia Pacific Interfinish '94*, Melbourne, Vic., Australia, October 1994, Institute of Metal Finishing, Vol II, 6-11.
- [21] H. Terryn: *ATB Metall.*, 1998, 38 (4), 41-49.
- [22] O.O. Knudsen, A. Bjorgum and B.S. Tanem: *ATB Metall.*, 2003, 43 (1-2), 175-180.
- [23] T. Schmidt-Hansberg and P. Schubach: *ATB Metall.*, 2003, 43 (1-2), 9-14.
- [24] J. Trolho, T. Schmidt-Hansberg and P. Schubach: *Aluminium extrusion*, 2003, 8 (3), 46-53.
- [25] R.L. Twite and P. Bierwagen: *Prog. Org. Coat.*, 1998, 33, 91-100.
- [26] C. Larson, J.R. Smith, G.J. Armstrong, *Trans. Inst. Met. Finish.*, 2013, 91, 120-132.
- [27] W. Pinc, S. Geng, M. O'Keefe, W. Fahrenholtz, T. O'Keefe, *Appl Surf. Sci.*, 2009, 255, 4061-4065.
- [28] G. Bierwagen, R. Brown, D. Battocchi, S. Hayes, *Prog. Org. Coat.*, 2010, 67, 195-208.
- [29] R. Grilli, The Surface Analysis Laboratory and Faculty of Engineering & Physical Science, University of Surrey, Surrey, UK, 2010, 17.
- [30] P. Traverso and G. Luciano: "EIS technique used to protective performance assessment of organic coatings: applicability in car component manufacturing", in "High performance Coatings for Automotive and Aerospace Industries", Nova Science Publishers, New York, USA, 2010, 385-398.
- [31] L. Belsanti, C. Bottino, G. Luciano, R. Stifanese, M. Toselli, P. Traverso, "Evaluation of anti-corrosive protection systems for aerospace applications in marine environment." Final Report of Research Contract, CNR n. 11958, 2013, 1-148.
- [32] R.H. Buchi, *Met. Finish.*, 2007, 37-40.
- [33] S.A. Kulinich, A.S. Akhtar, *Russian Journal of Non-Ferrous Metals*, 2012, 53 (2), 176-203.
- [34] R.B. Figueira, C.J.R. Silva, E.V. Pereira, *J. Coat. Technol. Res.*, 2015, 12 (1), 1-35.