

Deposition of cerium conversion coatings on AA2024-T3 aircraft alloy at fixed potentials

Tamara Pérez Gil, Stephan Kozhukharov, Christian Girginov

Abstract: *The present research is devoted on the potential abilities for deposition of Cerium Conversion Coatings (CeCC) as primer layers on AA2024-T3 aircraft alloy at potentiostatic regime. For this purpose, three potentials were selected as a driving force of the coating deposition process from diammonium pentanitrocerate solutions with the optimal concentrations of the cerium provider and deposition activator, determined in previous works. The correlation between the applied potentials and the morphological features of the obtained coatings was observed by Optical Metallographic Microscopy (OMM), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The analysis has provided the conclusion, that the applied potential possesses tremendous impact on the morphology of the obtained coating layers and probably alters the entire deposition mechanism.*

Key words: CeCC, AA2024-T3 aircraft alloy, electrochemical deposition, potentiostatic regime

INTRODUCTION

The specific function of the conversion coatings, in general, is to serve as primer layers that provide superior adhesion between the metallic substrate (i.e.: the fuselage material) and the exterior protective paint layers. Following the definition of Arenas et al, [1], it can be considered that the term "conversion coating" comprises each metal oxide layer deposited on a metallic surface, via whatever chemical or electrochemical process, that partially, or completely substitutes the native superficial metal oxide. Obviously, the performance of the conversion coatings is entirely predetermined by the technology, employed for their synthesis, and deposition. In the scope of the material science, the term "technology" includes the combination among all stages, processes and the corresponding methods that result in complete conversion of given raw or recycled materials and precursors, to industrial product with desirable features. In this sense, various methods were employed for CeCC deposition: spray deposition [2], spontaneous deposition by dip-coating [3 - 6], electrochemical deposition [7 - 9], reactive magnetron sputtering [10], etc.

Recently, Živković [9] reported successful electrochemical deposition at potentiostatic regime, and described the great importance of the applied potential on the features and the performance of the corresponding cerium oxide primer layers. These recent research works have predetermined the objectives of the present study.

The main task of the present work is to assess the influence of the potential applied as driving force for acceleration of CeCC deposition on AA2024-T3 aircraft alloy.

EXPERIMENTAL

Coating deposition procedures

The coatings were deposited on plates of AA2024-T3 commercial aircraft alloy, delivered by Southwest Aluminium Group CO.LTD (China). Prior to the depositions, the metallic substrates underwent alkaline etching in 50g/l. NaOH solution for two minutes at 50 °C, and subsequent immersion in diluted nitric acid – $\text{HNO}_3 - \text{H}_2\text{O} = 1:1$ v/v. for 10 minutes at ambient temperature. After cleaning by tap- and distilled water, each plate was assembled in a standard three-electrode flat cell [11], supplied by Metrohm [12]. The electric currents during the depositions were registered by Ag/AgCl-3M KCl reference electrode. The depositions were performed on circuit zones with 4 cm² geometrical surface area, exposed to 100 ml of deposition solution. It was prepared considering the optimal ingredient contents, established in the previous works [7, 8] performed on other alloy with similar chemical composition. The solution was composed by 0.03 mol/l. of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, in distilled water with 0.70 ml. addition of fresh 30% H_2O_2 as deposition activator. The deposition procedures were performed at potentiostatic regimes with: -0.5; -

1.0; -1.5 V, maintained by P/G-stat Autolab 30, product of Ecochemie (the Netherlands), with simultaneous recording of the currents during the deposition.

Morphological observations and characterizations

The optical metallographic microscopy was performed by commercial microscope Boeco (Germany), connected with a web-camera, at magnification rate of 40 times. It was followed by with SEM observation by TESCAN, SEM/FIB LYRA I XMU. The characterizations were completed by AFM observations, performed by scanning of square zones of the coatings with linear size of 49.5 μm , in dynamic regime at 170 kHz, with resolution 256 points per line to 256 lines, and speed of 2 – 5 seconds per line. The microscope was "Easyscan 2" produced by "Nanosurf", (Switzerland). It was supported by cantilever NCLR-10 aluminium coated pointprobe, product of "Nanoworld" (www.nanoworld.com).

RESULTS AND DISCUSSION

As is mentioned above, the currents were recorded during the depositions. The acquired curves are represented in Fig. 1.

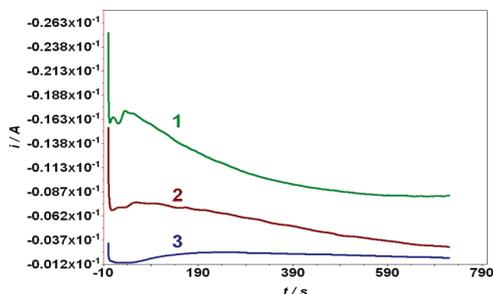


Fig. 1. Chronoamperometric curves acquired during coating depositions at different potentials: Curve 1: $E = -1.5$ V; Curve 2: $E = -1.0$ V; Curve 3: $E = -0.5$ V

Regardless the differences in their shapes, all curves are composed by sharp initial decays of the absolute current value. Such decays of the measured signal were described as a result of hydrogen evolution [7, 8], promoted by both acidic character of the solution and the cathodic polarization, or as a consequence of the electric double layer charging [13]. Rather probable cause for this decrease might be the OH^- ion electrogeneration, due to oxygen or/and peroxide reduction. After slight reversion, the current becomes decrease again. These signal alterations can be ascribed to subsequent nucleation and further coating nuclei growth. All the curves possess almost indistinguishable double minimums because the nucleation becomes initially at the most active S-phase intermetallics, and subsequently spreads on the less active inclusions, and the Al-oxide layer defects.

The main differences among the curves are their positions and the slopes of the second current decays. The highest applied potential corresponds to both the highest current and the sharpest slope. After the 590th second of deposition, the current across the coating becomes constant at -8.7 mA. After this moment, the film growth is probably suspended by diffusion obstructions, or it reaches a critical thickness, followed by partial coating detachment. On the other hand, almost any slope can not be observed at the lowest potential (curve 3), revealing almost complete absence of whatever film deposition. The intermediate potential value ($E = -1.0$ V) caused a gradual current decrement, from about -7.5 to -3.7 mA. The conjunction between the gradual slope of curve 2 and its twice lower final current, compared to this of curve 1 reveals gradual growth of dense and uniform layer. These facts lead to the assumption that the moderate potential value

predetermines a gradual growth of denser and more uniform conversion coating. This inference was confirmed by the morphological observations. Figure 2 represents photographs of the coatings deposited on AA2024-T3 plates at the respective potentials.

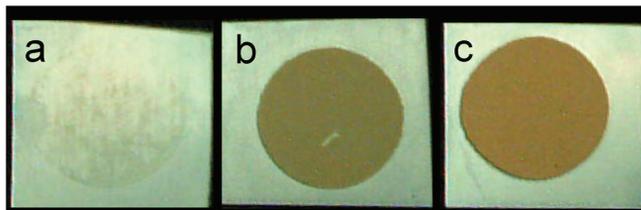


Fig. 2. Photographs of the metallic specimens after the CeCC electrodepositions at $E = -0.5$ V, position (a), $E = -1.0$ V, position (b), and $E = -1.5$ V, position (c),

From this figure becomes obvious that almost any deposition does not proceed at the lowest applied potential. Nevertheless, the excessive acceleration promoted by the highest potential has led to porous agglomerated CeCC layer with partial detachments, due probably to intensive hydrogen gas evolution, during the deposition at this potential, as can be seen from the optical micrographs in Fig. 3.

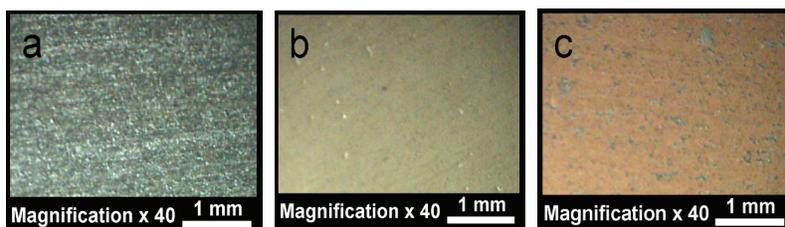


Fig. 3. Optical metallographic micrographs of the conversion coatings deposited at different potentials $E = -0.5$ V, position (a), $E = -1.0$ V, position (b), and $E = -1.5$ V, position (c),

Principally, the SEM method enables much higher magnifications than the optical microscopy. This method was used for obtaining of much more detailed image for the superficial morphology of the coating, deposited at the moderate potential (Fig. 4).

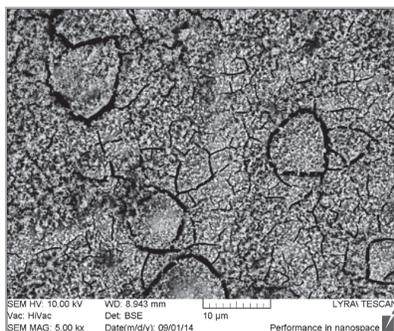


Fig. 4. SEM image of the CeCC deposited at $E = -1$ V

From the SEM micrograph becomes obvious that the coating deposited at the intermediate potential possesses uniformly distributed structure, similar to the reported in the literature [2, 5, 7, 8, 14, and 15].

The AFM observations confirmed the above mentioned statements, remarking that the densest and the most uniform conversion layer, obtained by potentiostatic electrochemical deposition at -1V, possesses fine grained structure and uniform distribution, as is shown in Fig. 5.

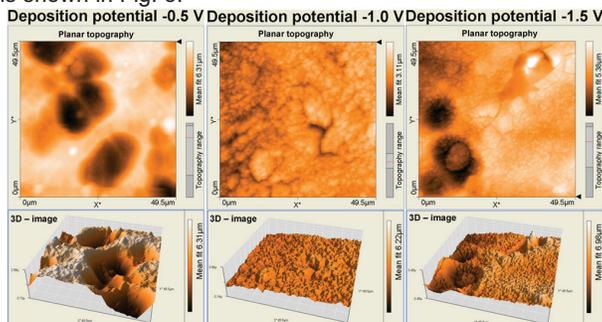


Fig. 5. Topographical and 3D images of CeCC deposited at potentiostatic regime

The observations performed by Atomic Force Microscopy complete the morphological observations in the present work, undoubtedly confirming all the assumptions and inferences done above. The images in Figures 2, 3 and 5 for the coating deposited at -0.5 V reveal almost uncovered metallic surface, identical to the described in previous works [16, 17]. There is also clear concordance among Figures 3, 4 and 5, regarding the specimen prepared at moderate conditions. Finally, Figure 5 proves the presence of layer detachment areas, observed in Fig. 3, which is caused by the accelerated film growth, promoted by the relatively high potential (i.e. -1.5 V).

CONCLUSIONS

The comparative morphological assessment executed during the present research has led to the following general conclusions:

- There is complete concordance among the results of the analytical methods used during the present research activities.
- Among the potentials selected for cathodic potentiostatic electrochemical deposition of Cerium Conversion Coatings from peroxide doped diammonium pentanitrocerate solution, the intermediated voltage ($E = -1.0$ V) has evinced to be the optimal.
 - Almost complete absence of deposits was established when 0.5V potential was used
 - The accelerated deposition at -1.5 V resulted in deposition of porous agglomerate film, accompanied by partial coating detachment.

Acknowledgements: The financial support by UCTM through project No: 11332-2014, entitled: "Incorporation of metals in porous Al_2O_3 matrices" is gratefully acknowledged.

REFERENCES

- [1] Arenas M., J. de Damborenea, "Generación de capas de conversión con elementos de tierras raras sobre acero galvanizado", Rev. Metal, Extra Volume, 2005, 433
- [2] Pinc W., S. Geng, M. O'Keefe, W. Fahrenholtz, T. O'Keefe, "Effects of acid and alkaline based surface preparations on spray deposited cerium based conversion coatings on Al 2024-T3", Appl. Surf. Sci. 255, 2009, 4061 – 4065.
- [3] Rivera B. F., B. Y. Johnson, M.O'Keefe, W.G. Farenholz, "Deposition and characterization of cerium oxide conversion coatings on aluminum alloy 7075-T6", Surf. Coat. Technol. 176, 2004, 349 – 356

[4] Kozhukharov S., O. F. Acuña, M. S. Machkova, V. Kozhukharov, "Influence of buffering on the spontaneous deposition of cerium conversion coatings for corrosion protection of AA2024-T3 aluminum alloy", *J. Appl. Electrochem.*, 44, 2014, 1093 – 1105.

<http://link.springer.com/article/10.1007/s10800-014-0718-7>

[5] Rodríguez D. S., S. Kozhukharov, M. Machkova, V. Kozhukharov, "Influence of the deposition conditions on the properties of D16 AM clad alloy, dip-coated in Ce-containing baths", *Bul. Chem. Commun.* 45, Spec. issue-A, 2013, 24 - 32. http://www.bcc.bas.bg/BCC_Volumes/Volume_45_Special_A_2013/BCC-45-SE-A-24-32.pdf

[6] Jegdić B., L. Živković, J. Popić, J. Bajat, V. Mišković-Stanković, "Electrochemical methods for corrosion testing of Ce-based coatings prepared on AA6060 alloy by the dip immersion method", *J. Serb. Chem. Soc.* 78, 2013, 997 – 1011.

[7] Ayuso J. A., S. Kozhukharov, M. Machkova, V. Kozhukharov, "Electrodeposition of cerium conversion coatings for corrosion protection of D16 AM clad alloy", *Bul. Chem. Commun.* 45, Spec. Issue-A, 2013, 33 - 40.

[8] Kozhukharov S., J.A.P. Ayuso, D.S. Rodríguez, O.F. Acuña, M. Machkova, V. Kozhukharov, "Optimization of the basic parameters of cathodic deposition of Ce-conversion coatings on D16 AM clad alloy", *J. Chem. Technol. Metall.* 48, 2013, 296 – 307. http://www.uctm.edu/journal/j2013-3/11-Stefan_Kojukharov-296-307.pdf

[9] Živković L. S., J.P. Popić, B.V. Jegdić, Z. Dohčević-Mitrović, J.B. Bajat, V.B. Mišković-Stanković, "Corrosion study of ceria coatings on AA6060 aluminum alloy obtained by cathodic electrodeposition: Effect of deposition potential", *Surf. Coat. Technol.* 240, 2014, 327 – 335.

[10] Ershov S., M.E. Druart, M. Poelman, D. Cossement, R. Snyders, M.-G. Olivier, "Deposition of cerium oxide thin films by reactive magnetron sputtering for the development of corrosion protective coatings", *Corros. Sci.* 75, 2013, 158 – 168.

[11] International Standard: ISO 16773-2: 2007 (E)

[12] Website: www.metrohm.bg

[13] Bard A. J., L. R. Faulkner, "Electrochemical methods, fundamentals and applications" 2th ed. Wiley New York 2001 ISBN 0-471-04372-9

[14] Zhao D., J. Sun, L. Zhang, Y. Tan, "Corrosion behavior of rare earth cerium based conversion coating on aluminum alloy", *Journal of Rare Earths*, 28, 2010, 371 – 374

[15] Heller D. K., W. G. Fahrenholtz, M. J. O'Keefe, "The effect of post-treatment time and temperature on cerium-based conversion coatings on Al 2024-T3", *Corros. Sci.* 52, 2010, 360 – 368.

[16] Matter E. A., S. V. Kozhukharov, M. S. Machkova, "Effect of preliminary treatment on the superficial morphology and the corrosion behaviour of AA2024 aluminum alloy", *Bul. Chem. Commun.* 43, 2011, 23 – 30. http://www.bcc.bas.bg/bcc_volumes/Volume_43_Number_1_2011/Volume_43_Number_1_2011_PDF/2011-43-1_3.pdf

[17] Matter E., S. Kozhukharov, "Correlation between preliminary pretreatments and the behaviour of AA-2024 – aluminium alloy in 3.5% NaCl model corrosive medium", *Ann. Proceeds, "Angel Kanchev" University of Rousse (Bulgaria)* 49, 9.1, 2010, 14 – 19. <http://conf.uni-ruse.bg/bg/docs/cp10/9.1/9.1-2.pdf>

About the authors:

Tamara Pérez Gil – M.Sc. student in University of Vigo (Spain); www.uvigo.es

Dipl. eng. Stephan V. Kozhukharov Ph. D., UCTM – Sofia (Bulgaria); www.uctm.edu,

e-mail: stephko1980@abv.bg

This paper has been reviewed