

FRI-21-P-CT(R)-05

---

**SURFACE Zn-INCLUSION IN PHOSPHATE TREATED CERIUM CONVERSION  
COATINGS DEPOSITED ON AA2024-T3 AIRCRAFT ALLOY**

---

**Stephan Kozhukharov,**

**Christian Girginov**

University of Chemical Technology and Metallurgy, BG

E-mail: stephko1980@abv.bg;

E-mail: girginov@uctm.edu

**Ivalina Avramova**

Institute of General and Inorganic Chemistry, BG

Bulgarian Academy of Sciences

E-mail: iva@svr.igic.bas.bg

**Mariano Milanes**

Student

University of Chemical Technology and Metallurgy, BG

E-mail: marianomilanes1987@gmail.com

**Abstract:** This paper is focused on the determination of the Zn-inclusion in phosphate finishing sealing of Cerium Conversion Coatings (CeCC), deposited on AA2024-T3 aircraft alloy. For this purpose, metallic plates were submitted to a sequence of procedures: preliminary treatment, CeCC deposition and final phosphate film sealing. In order to determine the possibility for Zn inclusion inside the obtained multilayered structure, three advanced instrumental analytical techniques were used for the final film characterization: Scanning Electron Microscopy (SEM), combined by Energy Dispersion X-ray (EDX) analysis and X-ray Photoelectron Spectroscopy (XPS). The latter analytical technique was employed for the determination of the oxidation states of the coating components, as well as the nature of the chemical bonds between them. Furthermore, this advanced instrumental technique enables to establish the exact chemical compounds, formed during the CeCC deposition and the subsequent phosphatation. The results show that the Zn compound does not include in the phosphate finishing layer, but rather forms coarse crystals on its surface.

**Key words:** AA2024 aircraft alloy, CeCC, Phosphatation, Dopants, SEM, EDX, XPS

## INTRODUCTION

Recently, the need for removal of Cr(VI) compounds from the corrosion protection coating materials and technologies has arisen as a great challenge for the entire transport industry. The substitution of the widely used Chromium Conversion Coatings (CCC), by Cerium Conversion Coatings (CeCC) is an adequate and efficient response to this challenge [1].

On the other hand, the CeCC performance can be significantly improved by a final phosphatation procedure [2]. This procedure possesses obvious beneficial effects for the corrosion protection using various metals, such as Zn [3, 4]. In addition, the composition of the resulting phosphate layers can be varied by addition of various metallic ions, as is proposed by Ignatova et al. [5].

All these facts have inspired the present brief research on the possibility for integration of Zn compounds in a phosphate sealing film composition.

## EXPERIMENTAL

**Sample preparation:** The used substrates were AA2024-T3 metallic plates, which have undergone a sequence of procedures, divided into three stages: (i) preliminary treatment: NaOH etching, followed by desmutting in diluted HNO<sub>3</sub>; (ii) potentiostatic CeCC deposition: performed at -1 V vs. Ag/AgCl reference electrode, for 720 s in 0.03 mol dm<sup>-3</sup> (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>5</sub> aqueous solution with addition of fresh 30% H<sub>2</sub>O<sub>2</sub>, following the procedures described in [6]; (iii) finishing

phosphate CeCC sealing. Namely the latter procedure was the objective of the present research work. It was performed by immersion of the already CeCC-coated metallic samples for 30 min. at 90 °C in covered beakers, filled with the phosphatation solutions, whose compositions are given in Table 1.

Table 1. Compositions of the used phosphating solutions

Phosphating Solution code	Basic ingredient	Dopant
CeP (Zn)	0.03 mol dm <sup>-3</sup> (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	0.03mol dm <sup>-3</sup> Zn(NO <sub>3</sub> ) <sub>2</sub>
CeP (ref)	0.03 mol dm <sup>-3</sup> (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	-----

**Sample Characterization techniques:** In order to characterize the surface morphology and composition, two instrumental techniques were used: (i) Scanning Electron Microscopy (SEM), coupled with Energy Dispersion X-ray (EDX) spectroscopy. (ii) X-ray photoelectron spectroscopy (XPS) compositional analysis was applied in order to determine the surface composition.

The SEM observations were performed by TESCAN, SEM/FIB LYRA I XMU microscope, supported by Quantax 200 EDX detector of BRUKER. The XPS compositional analyses were executed by Kratos AXIS Supra with a monochromatic Al X-ray source. Each analysis started with a survey scan from 0 to 1200 eV, pass energy of 160 eV at steps of 1 eV with 1 sweep. For the high resolution analysis the number of sweeps was increased, the pass energy was lowered to 20 eV at steps of 100 meV.

The X-ray Photoelectron spectroscopy method was used for the investigation of the surface of cerium phosphate and cerium phosphate doped with Zn coating on AA2024-T3 type alloy. The C1s, O1s, Al2p, Ce3d, Na1s, N1s, P2p, as well as the Zn2p photoelectron lines were recorded and the obtained spectra were discussed. The O1s photoelectron line of cerium phosphate used for reference and cerium phosphate doped by Zn were subjected to deconvolution, using the XPSPEAK4.1 software.

## RESULTS AND DISCUSSION

The SEM/EDX observations have revealed very distinguishable surface morphology, revealing the impact of the Zn-dopant on the phosphatation procedure (Fig. 1).

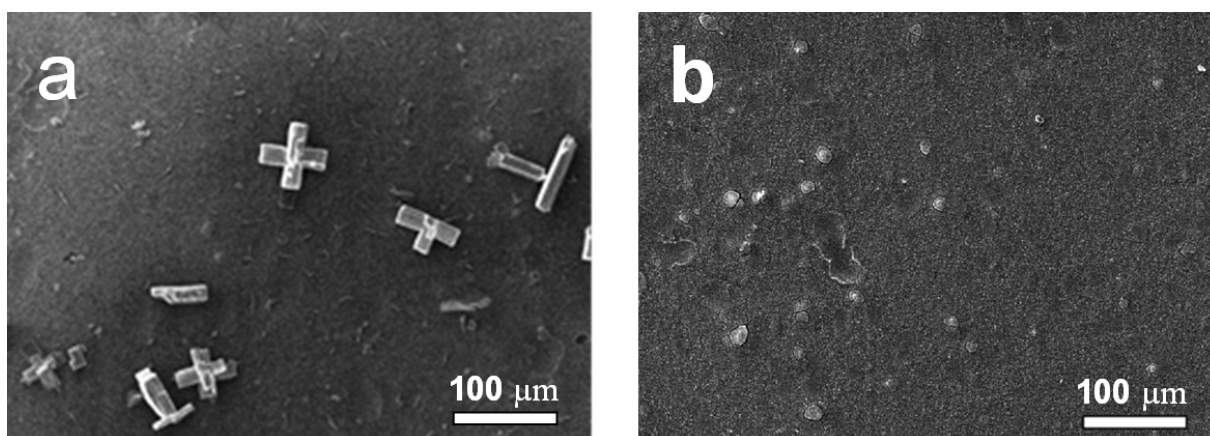


Fig. 1 Low resolution SEM images acquired for the the Zn doped (a) and the referent (b) specimens, at 500x magnification.

The low resolution SEM image for CeP(Zn) (Fig.1a) reveals rectangular and cross like coarse crystals randomly distributed on the entire phosphated CeCC coating surface. The respective image of the referent sample shows oval hills, probably formed predominantly on the copper containing

intermetallic inclusions, following the "island like growth" model, described by Aldykevich et al. [7], confirmed by Lau et al. [8]. In other words, the CeCC film growth initiates predominantly on the cathodically acting intermetallics inclusions in the basic alloy and spreads afterwards on the rest of the substrate surface area, until it covers the entire treated zone, following another mechanism, described by Conde et al. [9]. Using these concepts for CeCC growth mechanisms, can be explained both the occurrence of thicker layer hills and the uniform coverage of the remaining surface.

The subsequent phosphatation procedure results in uniform distribution of a thin phosphor-containing layer on the CeCC surface for both samples (Fig. 2).

The peculiar crystals in the case of the CeP(Zn) undoubtedly originate from the presence of the Zn-dopant in the phosphating solution. These crystals are probably formed on the thicker CeCC oval domains described above, since these are randomly distributed (Fig. 2).

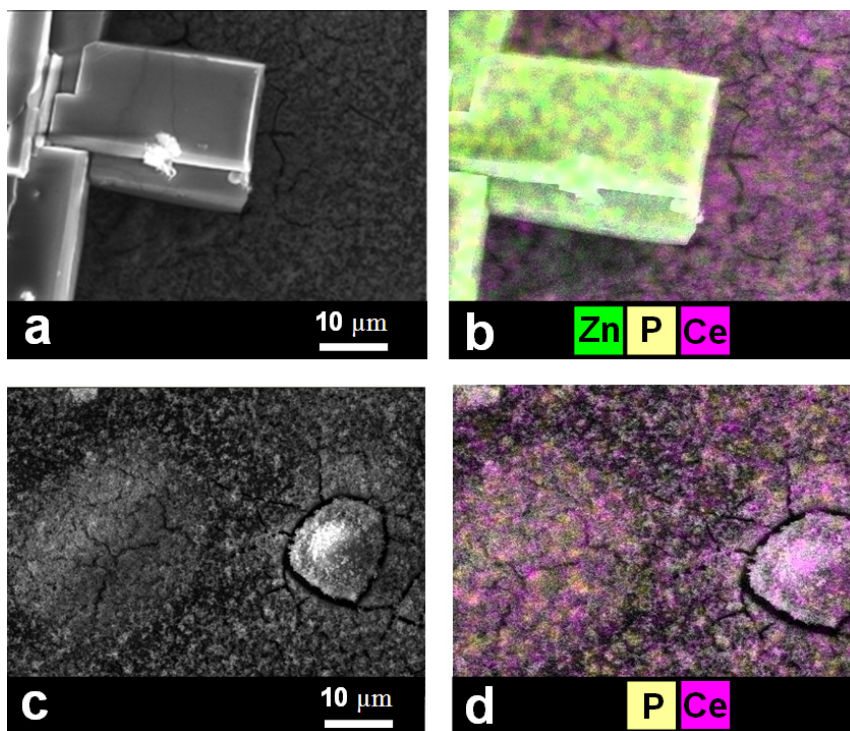


Fig. 2 High-resolution SEM images (a, c) at 5000x magnification and EDX maps (b, d) of CeP(Zn) samples (a, b) and CeP(ref) samples (c, d)

The EDX map analyses reveal that the crystals are composed of both Zn and P, revealing that the most probable composition is  $ZnH(PO_4)_2$ , and/or  $Zn_3(PO_4)_2$ .

Part of the results of the performed XPS analyses are presented in Fig. 3.

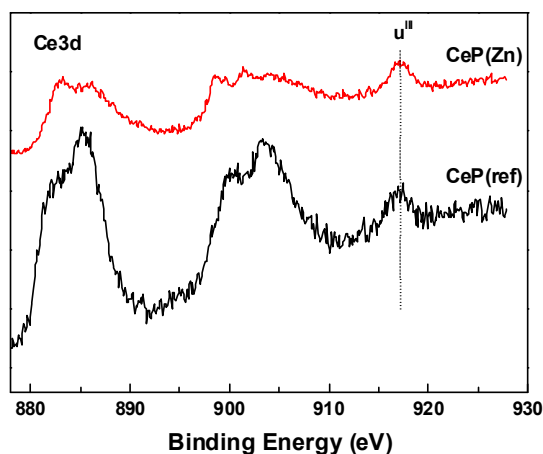


Fig. 3. Ce3d spectra acquired for the investigated coatings

From the above shown Ce3d spectra is obvious that the cerium in the pure cerium phosphate coating (CeP(ref) sample) is predominantly in Ce<sup>3+</sup> states. The Zn doping caused the change of the cerium chemical states to mostly Ce<sup>4+</sup>.

The amount of Ce(IV) in the oxide film was evaluated as a percentage of the area of the u<sup>III</sup> peak at about 916.8 eV to the total Ce3d peak area. Thus, the percentage of the u<sup>III</sup> peak with respect to the total Ce3d peak area varies from 0 to 14 %, while the Ce(IV) percentage to total amount of Ce varies from 0 to 100% [10]. As a result of the explained above calculations we obtained the following result: in Ce<sup>4+</sup> state are 25.65 % of the total cerium incorporated in the CeP(ref) coating and 67.21% in the Zn doped coating CeP (Zn), respectively.

The first peak of the complex O1s spectra of the studied coatings as a result of the fitting is situated around 529.5 eV and is associated with Ce-O bonds. A small shift to higher binding energy for the Zn doped cerium phosphate was observed, which could be due to a formation of mixed oxide, as well as separate existence of CeO<sub>x</sub> and ZnO on its surface. The second peak at 531.2 eV belongs to oxygen in CePO<sub>4</sub> [11].

In the case of Zn doping the second photoelectron peak most probably is also due to presence of oxygen vacancies in the ZnO lattice on the surface. The third peak at around 532.5 eV is associated with oxygen in Ce-OH and Zn-OH bonds. Here, it is worth noticing that the most intensive peak is at 531.2 eV, which means that CePO<sub>4</sub> was formed on both film surfaces of the investigated coatings [12].

The P2p photoelectron line for all investigated coatings is situated at 133.3 eV, value typical for phosphorus in CePO<sub>4</sub> compounds [11]. Additionally the existence of the P<sub>2</sub>O<sub>5</sub> is also possible because the coatings are not thermally treated.

The Zn element is also present on the surface in the oxide state Zn<sup>2+</sup>. Some quantity of aluminum from the substrate was also detected, which is most probably due to the surface roughness, existence of pores in the coatings or to their different thicknesses.

## CONCLUSIONS AND FUTURE WORK

From the analysis of the acquired results, the following inferences can be done:

Both samples show uniform coverage of the metallic surface by the deposited CeCC coatings.

The referent sample shows oval hills, probably formed predominantly on the copper containing intermetallic inclusions, in accordance with the "island like growth" model, followed by a gradual coverage of the remaining part of the surface.

The Zn doped phosphate coating reveals rectangular and cross like coarse crystals, randomly distributed on the entire phosphated CeCC coating surface.

The EDX maps show clear segregation among the elements composing the film. The crystals observed on the CeP(Zn) surface are composed of both Zn and P, presupposing the formation of crystalline ZnH(PO<sub>4</sub>)<sub>2</sub> and/or Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.

From the XPS analysis, it can be concluded that the Zn-doping causes oxidation of the cerium chemical states to mostly Ce<sup>4+</sup>, whereas the cerium in the pure cerium phosphate coating is predominantly in Ce<sup>3+</sup> states. Thus, the amount of the Ce(IV) compounds (in % from the total incorporated cerium) in Ce<sup>4+</sup> state is: 25.65 % for the reference CeP(ref) and 67.21% for the Zn doped one (CeP(Zn)).

Both coatings are composed by a mixture of Zn and Ce oxides and hydroxides, with predominance of CePO<sub>4</sub>. Probably, more uniform compositions are achievable by subsequent thermal treatment, which will be the object of further investigations.

**Acknowledgements:** The authors gratefully appreciate financial support via the Bulgarian National Scientific Research Fund DFNI, under contract T02-27 / 2014

**REFERENCES:**

- [1] Kozhukharov, S. V. (2016) Deposition of Environmentally Compliant Cerium-Containing Coatings and Primers on Copper-Containing Aluminium Aircraft Alloys, PUBLISHED IN: Biobased and Environmental Benign Coatings (eds A. Tiwari, A. Galanis and M. D. Soucek), John Wiley & Sons, Inc., Hoboken, NJ, USA. doi: 10.1002/9781119185055.ch2
- [2] 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
- [3] Ivanova D.I., Phosphating of zinc surfaces in zinc-calcium solutions, *Bul. Chem. Commun.* 43 (2011) 54 – 59
- [4] Tumbaleva Y., D. Ivanova, L. Fachikov, Effect of the  $P_2O_5:NO_3$  – ratio on the zinc phosphate coating formation, *J. Univ. Chem. Technol. Met.* 46 (2011) 357 – 362
- [5] Ignatova K., S. Kozhukharov, L. Vladimirov, M. Milanes, Impact of the electroplating regime on the chemical composition of Ni-Co-P based coatings in non-complexing acidic electrolyte, Annual proceedings of “Angel Kanchev” University of Ruse (Bulgaria), 54 (2015), 84 – 88
- [6] Gil T. P., S. Kozhukharov, C. Girginov, Deposition of cerium conversion coatings on AA2024-T3 aircraft alloy at fixed potentials, Annual proceedings of “Angel Kanchev” University of Ruse (Bulgaria), 53 (2014) 9-13
- [7] Aldykiewicz A. J., A. J. Davenport, H. S. Isaacs, Studies of the Formation of Cerium-Rich Protective Films Using X-Ray Absorption Near-Edge Spectroscopy and Rotating Disk Electrode Methods, *J. Electrochem. Soc.* 143 (1996) 147-154
- [8] Lau D., A.M. Glenn, A.E. Hughes, F.H. Scholes, T.H. Muster, S.G. Hardin, Factors influencing the deposition of Ce-based conversion coatings, Part II: The role of localised reactions, *Surf. Coat. Technol.*, 203 (2009) 2937-2945
- [9] Conde A., M.A. Arenas, A. de Frutos, J. de Damborenea, Effective corrosion protection of 8090 alloy by cerium conversion coatings, *Electrochim. Acta* 53 (2008) 7760-7768
- [10] J.Z. Shyu, K. Otto, W.L.H. Watkins, G.W. Graham, R.K. Belitz, H.S. Gandhi, Characterization of Pd/ $\gamma$ -alumina catalysts containing ceria, *J. Catal.* 114 (1988) 23-33
- [11] J.M. Pemba-Mabiala, M. Lenzi, J. Lenzi, A. Lebugle, XPS study of mixed cerium-terbium orthophosphate catalysts, *Surf. Interface Anal.* 15 (1990) 663-667
- [12] Zhang H., Y. Zuo, The improvement of corrosion resistance of Ce conversion films on aluminum alloy by phosphate post-treatment, *Appl. Surf. Sci.* 254 (2008) 4930-4935

**About the authors**

Dipl. Eng. Stephan Kozhukharov, Ph. D., University of Chemical Technology and Metallurgy, 8 Kliment Okhridsky blvd. 1756 – Sofia (Bulgaria), e-mail: stephko1980@abv.bg

Assoc. Prof. Ivalina Avramova, Ph. D., Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad G. Bonchev str., Block 11, e-mail: iva@svr.igic.bas.bg

Assist. Prof. Christian Girginov, Ph. D., University of Chemical Technology and Metallurgy, 8 Kliment Okhridsky blvd. 1756 – Sofia (Bulgaria), e-mail: girginov@uctm.edu

Mr. Mariano Milanes, B. Sc. Student, University of Chemical Technology and Metallurgy, 8 Kliment Okhridsky blvd. 1756 – Sofia (Bulgaria), e-mail: marianomilanes1987@gmail.com