



## Corrosion inhibiting cerium compounds for chromium-free corrosion protective coatings on AA 2024



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with cerium nitrate in combination with acetylacetone.

### Summary

Due to the upcoming ban of chromium-containing corrosion protection coatings in the near future, there is a worldwide effort to find a replacement for chromium as a corrosion inhibitor that also exhibits self-healing properties in scratches but without the negative effects like health and environmental hazards. In the present study promising results to achieve this goal are shown by using cerium compounds incorporated into an organic-inorganic hybrid material produced by the sol-gel process. Cerium compounds like cerium nitrate, cerium nitrate plus acetylacetonate, cerium acetylacetonate, and cerium sulphate were incorporated in sol-gel coating systems. The corrosion protection properties of these coatings were determined by means of Electrochemical Impedance Spectroscopy (EIS) and in a conventional salt spray test. Furthermore, the leaching behaviour of the coatings was examined via Optical Emission Spectrometry (OES). Significant hints for self healing properties were obtained with a hybrid system doped

### Introduction

The AA 2024-T3 stands for a frequently used aluminium alloy in the aerospace industry. It combines relative high tensile strength (11 times higher than pure aluminium) with low density. The alloy consists of up to 4.9 wt% copper, 0.9 wt% manganese, 1.8 wt% magnesium, 0.5 wt% silicon, 0.5 wt% iron, and aluminium [1]. The high copper content makes the material very sensitive to corrosion attack since the copper-rich intermetallics act as local cathodes which promote the anodic dissolution of the surrounding aluminium [2]. State of the art in the corrosion protection of aluminium alloys is the use of chromium (VI)-containing coatings. Due to the toxicity and carcinogenicity of chromium (VI) alternative corrosion protection coatings have to be developed.

According to the work of several groups [3-6] the use of cerium compounds appears to be a feasible alternative for the replacement of chromium. Mansfeld et, al. proposed the treatment of aluminium in cerium nitrate solutions [7], in which the substrates are kept for several hours

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at temperatures close to the boiling point of the solution. The long process duration appears to be impractical for industrial use, therefore in this study the use of cerium compounds in a sol-gel derived hybrid organic-inorganic coating will be discussed.

## Experimental Setup

### Synthesis of coating material

An inorganic-organic hybrid sol was synthesized according to reference [8]. In summary, the sol was synthesized by mixing and hydrolysing three solutions that had been prepared separately. Firstly, tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS) and SiO<sub>2</sub> nanoparticles, as components of the inorganic network, were mixed and hydrolysed by concentrated hydrochloric acid (HCl). Secondly, for creation of the organic substructure and crosslinking with the inorganic network, 3-glycidoxypropyltrimethoxysilane (GPTS) was used. To assist hydrolysis, 0.1 M hydrochloric acid was added as a catalyst. At this stage the cerium compounds were added to the solution at cerium concentrations of 2.5 wt% and 4 wt%, calculated with respect to the solid material. Thirdly, the organic substructure of the hybrid

material, consisting of 2,2'-bis-(4-hydroxyphenyl)-propane (BPA), was dissolved in an organic solvent. Finally, after completing the hydrolysis, the three solutions were mixed together. Prior to coating, the organic crosslinking was started by adding 1-methylimidazole to start the organic polymerisation.

The cerium compounds used for these experiments were cerium acetylacetonate (Ce[acac]<sub>3</sub>), cerium nitrate, and cerium sulphate. Additionally cerium nitrate was dissolved in ethanol and mixed with an equimolar amount of acetylacetone (Hacac). This mixture was also added to the coating material. The samples of this material were labelled cerium nitrate plus acetylacetonate. These compounds were added to the coatings in order to achieve a cerium concentration of 2.5 wt% related to the solid coating material. Only the cerium nitrate plus acetylacetonate doped coating system had a higher solid content of 4 wt%.

### Substrates and Pre-treatments

Aluminium alloy 2024-T3 was used for deposition of single layer sol-gel coatings. The aluminium samples were degreased with acetone, cleaned with Metaclean T2001 (Chemie



Vertrieb Hannover, Germany), and afterwards etched in an alkaline cleaner (Turco Liquid Aluminetch Nr. 2 from Turco Chemie, Germany). Subsequently the substrates were desmuted with Turco Liquid Smut-go NC. The coatings were applied by dip-coating with a coating velocity of 9 mm/s and cured at 120 °C for 4 h.

### Characterization of the coated samples

The corrosion protection performance of the samples was characterized by means of the neutral salt spray test according to DIN 50021. The backside and the edges of the samples were covered with adhesive tape and beeswax respectively. An artificial scratch was applied in the corrosion protection coating according to Van Laar [9] in order to examine the delamination behaviour. The samples were taken out of the test once a week in order to take photos with a digital camera with a resolution of 0.07 Pixel per millimeter. These images were then used to evaluate the corrosion protection by measuring the time in the salt spray test until the first occurrence of corrosion marks

The long-term barrier performance of the coated samples were tested

in a 3.5 wt% sodium chloride solution via Electrochemical Impedance Spectroscopy (EIS) using a potentiostat 2273 (AMETEK Princeton Applied Research, Tennessee, US). A three-electrode electrochemical cell with a platinum sheet and a saturated calomel electrode as counter and reference electrode, respectively, was used for the measurements. The sample testing area exposed to the electrolyte was 6.6 cm<sup>2</sup> and the signal amplitude was 10 mV with a frequency range between 5 mHz and 485 kHz. Electrochemical impedance spectra were recorded regularly from each coated sample. The impedance values from the low frequency range can provide information about the self-healing properties of a coating-system [10]. For this reason in particular the impedance values at 0.01 Hz were considered in this work and were plotted against the immersion time.

Following the EIS measurements, Tafel plots ( $\pm 20$  mV from the open circuit potential (OCP)) were carried out for determining the corrosion current density of these coated samples.

The possibility that an inhibitor is released from a coating and migrates to a scratched area is a basic requirement for self-healing properties of a

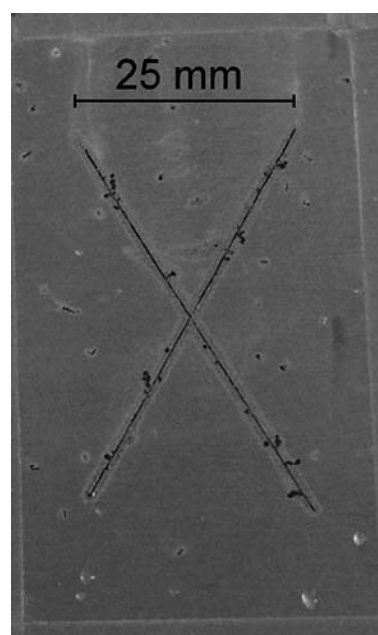


Fig. 1: Coating material without cerium compounds after 330 h salt spray test

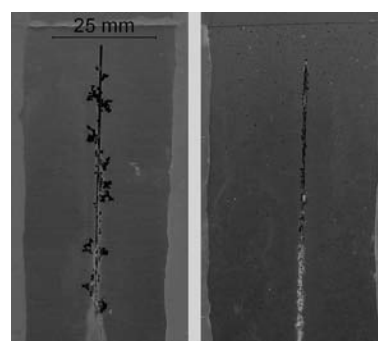


Fig. 2: Cerium sulphate (left) and cerium acetylacetonate (right) filled coatings after 336 hours salt spray test

coating. For this reason the leaching of cerium out of the coatings after certain periods of time (2.5, 24, 96, and 120 h) in aqueous media was determined via Inductively Coupled Plasma / Optical Emission Spectrometer (ICP/OES) ULTIMA 2 (HORIBA Jobin Yvon GmbH, Munich, Germany). Each double-sided coated sample with a total coating area between 44 cm<sup>2</sup> (cerium nitrate plus acac) and 50 cm<sup>2</sup> (Ce[acac]<sub>3</sub>) was cut in four pieces and was immersed in 100 ml bidest water. To avoid a direct contact of the sample pieces in the immersion medium, the edges were coated with beeswax. After a certain time (2.5, 24, 96, 120h), a water sample of 10 ml was taken out of the immersion medium and subsequently analysed via ICP/OES. The coating thicknesses were measured by means of a magnetic induction method with a PERMASCOPE (Helmut Fischer GmbH & Co, Sindelfingen, Germany).

## Results

The coating system without cerium compounds showed first corrosion marks after 170 hours. After 336 hours of neutral salt spray test corrosion in the general area as well as sub-surface migration at the artificial scratch is clearly detectable (figure 1).

While the cerium sulphate containing coatings showed creepage at the artificial scratch after 336 h of salt spray testing, the cerium acetylacetonate filled coatings exhibited pitting all over the substrate after the same time. A comparison of the cerium sulphate, and cerium acetylacetonate filled coatings after 336 hours salt spray test is displayed in figure 2. Comparing cerium sulphate and cerium acetylacetonate filled coatings with unfilled ones demonstrates a slightly reduced amount of pitting (figure 1 and figure 2). In the case of cerium nitrate the substrate remained without traces of corrosion for 700 hours (figure 3).

The coating filled with cerium nitrate plus acetylacetonate showed no corrosion marks for 1800 hours of neutral salt spray testing. A comparison of images of this coating system after 336 h and 1800 h respectively is shown in figure 4.

The coating thickness is in the range of 10 µm for all samples (table 1). Therefore the influence of the coating thickness on the corrosion protection properties is negligible.

Sample name      Coating thickness

- Unfilled coating                      9 µm
- Cerium nitrate                              13 µm

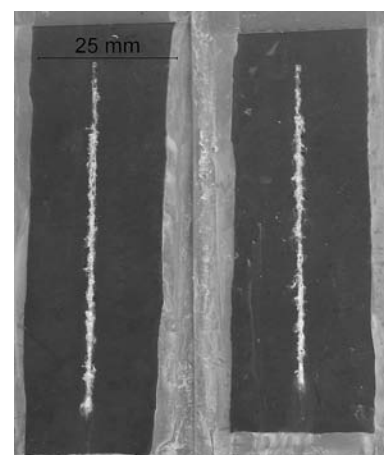


Figure 3: Photo of cerium nitrate containing coatings after 750 hours salt spray test.

Sample name	Coating thickness
Unfilled coating	9 µm
Cerium nitrate	13 µm
Cerium acetylacetonate	9 µm
Cerium sulphate	8 µm
Cerium nitrate plus acac	11 µm

Table 1: Measured coating thicknesses



- Cerium acetylacetonate 9  $\mu\text{m}$
- Cerium sulphate 8  $\mu\text{m}$
- Cerium nitrate plus acac 11  $\mu\text{m}$

The Tafel plots of these coating systems after one hour and 40 minutes immersion in a 3.5 wt% sodium chloride solution are shown in figure 5. The largest corrosion current density of about  $5 \times 10^{-6} \text{ A / cm}^2$  as well as the lowest OCP of 0.84 V showed the cerium sulphate doped coating system. The second lowest corrosion current density of around  $10^{-8} \text{ A / cm}^2$  but the highest OCP of -0.15 V exhibited the cerium nitrate plus acac coating system. The unfilled and the Ce acac doped coating system showed similar corrosion current densities of  $2 \times 10^{-10} \text{ A / cm}^2$  and  $4 \times 10^{-10} \text{ A / cm}^2$  as well as similar OCPs of 0.61 V and 0.65 V, respectively. The cerium nitrate coating system showed the same corrosion current density as the Ce acac coating system but a considerably higher OCP of -0.18 V.

The long-term impedance modulus behaviour of the tested coating systems, measured via EIS, is shown in figure 6. Altogether, the unfilled coating system exhibited the highest impedance modulus of up to 180  $\text{M}\Omega\text{cm}^2$  in comparison with the cerium salt doped coating systems, which only have impedance modu-

lus values under 9  $\text{M}\Omega\text{cm}^2$ . The unfilled coating system, the cerium nitrate and the Ce acac doped coating system showed a relatively fast decreasing impedance modulus in time. In contrast the cerium nitrate plus acac coating system exhibit at the beginning an increasing impedance modulus and then only a slow decrease of the impedance modulus in time. The experiment of the cerium sulphate doped coating system is still running.

The results of the leaching experiments are presented in figure 7. Leaching of cerium was only proven for the cerium nitrate plus acac doped coating system after 96 and 120 h immersion time. The other coating systems are apparently not able to leach out their cerium ions.

## Discussion

The cerium compounds examined in this study were selected in order to compare cerium compounds of different solubility with cerium nitrate, which was proposed for corrosion protection on aluminium by Mansfeld [7]. Cerium nitrate and cerium sulphate are soluble in water, while cerium acetylacetonate has only a limited solubility in water due to the chelating properties of acetylacetonate

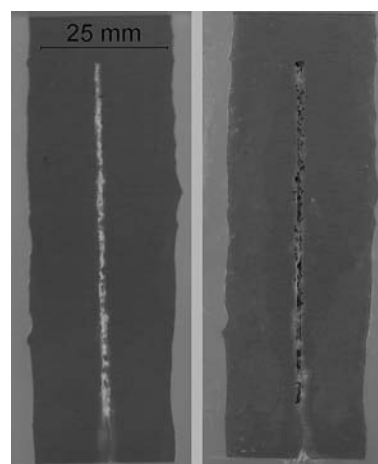


Fig. 4: Image of cerium nitrate plus acetylacetonate filled coating after 336 h (left) and 1800 h salt spray testing

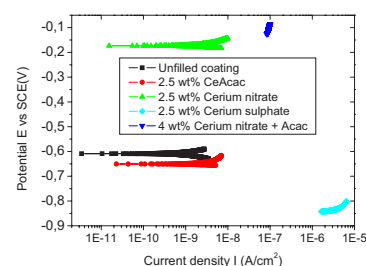


Fig. 5: Tafel plots ( $\pm 20 \text{ mV}$  vs. OCP) of the four different cerium compound-doped coating systems as well as the unfilled coating.

te. The limited solubility of cerium acetylacetonate may be an advantage, because the dissolution of the corrosion inhibitor may cause porosity which then weakens the barrier properties of the coating, or on the other hand the inhibitors may be leached to the environment without fulfilling their purpose of corrosion inhibition, if the inhibitor is leached out of the coating because of the high solubility.

The different behaviour of the coatings can be explained partially by the differences in solubility. Because of the limited solubility of Cerium acetylacetonate, only a very small amount of cerium will be released from the coating in order to block corrosion sites. In the case of the soluble cerium compounds cerium sulphate and cerium nitrate, the reason for the difference in corrosion protection can be found in the critical inhibitor concentration. As published by Bhattamishra and Banerjee it is necessary that in the case of cerium sulphate a critical concentration of about 500 ppm inhibitor in aqueous 3.5 % NaCl solution is exceeded to facilitate efficient corrosion protection, while even low amounts of cerium nitrate increase the corrosion behaviour of aluminium [3]. In the leaching experiments

it turned out that even in the case of cerium nitrate, which showed good performance in the salt spray test, the amount of inhibitor in the diluent was below the limit of detection of the ICP/OES. Only in the case of the cerium nitrate plus acac samples the cerium concentration was higher than the limit of detection.

Concerning the electrochemical examination, the addition of cerium nitrate resulted in ennoblement, i.e. an increase of OCP, of the coated specimens. The absence of the cathodic branch of the cerium nitrate plus Hacac and the cerium sulphate coating system is due to the reduction of metal ions of the passive film or the barrier oxide layer, which resulted in a shift of the OCP toward negative directions [11]

Relating to the results of the SST, leaching, and EIS measurements the best performance of all samples examined exhibited the cerium nitrate plus Hacac coating system in particular in contrast to the cerium nitrate doped coating system without Hacac. It showed the best performance in the salt spray test and was the only system in which a leaching of cerium could be proven. Furthermore, only this coating system shows at the beginning of the long-term impedance modulus measurements an increasing

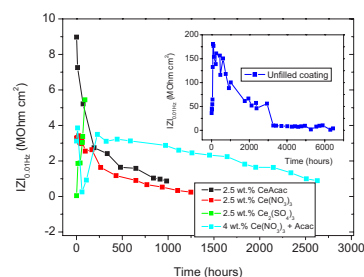


Fig. 6: Impedance modulus  $Z$  (at 0.01 Hz) against the immersion time in a 3.5 wt.% sodium chloride solution of four different cerium salts doped coating systems as well as an unfilled coating measured via EIS.

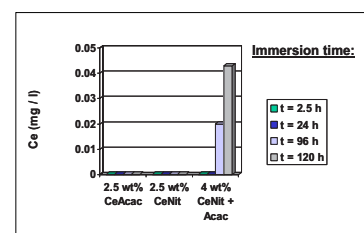


Fig. 7: Contents of cerium in dependence on the immersion time of three different cerium salts doped coating systems as well as the undoped coating system in aqueous media measured by means of Optical Emission Spectrometry.



of the impedance modulus and at the same time only a slightly decrease of that value in time. Altogether, the presented results can be taken as clear evidence of self-healing properties of the hybrid coating doped with cerium nitrate in combination with acetylacetone on AA2024.

The findings presented in this paper may be interpreted as evidence, that in the case of the cerium nitrate plus acac doped coating system the amount of released corrosion inhibitors is sufficient for efficient corrosion protection in contrast to the cerium nitrate, cerium sulphate, and cerium acetylacetonate doped coating systems. However, up to now it is not clear if this behaviour is caused by the higher cerium concentration, the beneficial combination of cerium nitrate with acac, or a mixture of both. The effect of the addition of acetylacetone to coating systems with varying cerium nitrate concentrations is subject of currently running experiments.

## Conclusions

Cerium nitrate in combination with acetylacetone is an efficient corrosion inhibitor, when used as additive to hybrid organic-inorganic coatings. The results of the salt spray test, le-

aching experiments, and EIS measurements show clear evidence of self-healing behaviour in that coating system during the first 300 h. Cerium nitrate is according to the salt spray test performance the second best additive to the hybrid coating system used in this study.

The other cerium compounds examined show only limited corrosion protection abilities due to the results of the electrochemical- and salt spray tests.

## Outlook

Further experiments will be conducted in order to analyse the leaching behaviour of the coatings. New pathways of storing corrosion inhibitors in the coating will be tested soon.

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## Microstructure investigation of reflective coatings interference multilayers produced by sol-gel method



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### Annotation

The results presented here have also been published during the EURO-CORR 2007.

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### 1. Introduction

Reflective and antireflective coatings play an important role in different branches of industry like optical devices, solar panels, medical devices (endoscopes), architecture, etc. The reason for this is the increase or reduction of transmittance or reflectance of the surfaces to the desired values. Transmittance and reflectance have to be optimized at different wavelengths depending on the application of the products.

There are different methods to change the reflectance of the surfaces: a) reflectance of the surface can be increased by coating the surface with metal (Al, Ag); b) reflectance of the surface can be decreased by coating the surface with moth eye pattern (coating with micro roughness on the surface or etching of the surface); c) reflectance of the surface can be decreased or increased by coating the surface with interference multilayers (the layers contain low and high refractive index materials). This paper is focused on the interference multi-