"PARTNERING FOR SHARED SOLUTIONS TO COMMON ENVIRONMENTAL PROBLEMS"

ENVIRONMENTALLY FRIENDLY PRE-TREATMENTS FOR ALUMINIUM ALLOYS

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Aluminium Alloys for the Aeronautical Industry (e.g. AA 2024-T3)

➔They are light, with good uniform corrosion resistance and fatigue resistance.

➔They have low pitting corrosion resistance.

➔They need protection before use, e.g., paint application.

➔Application of paint requires:

- A resistant and stable interface, promoting adhesion between the paint and the substrate;

- For this purpose, surface pre-treatments are used, being traditionally based on chromate.

Nominal Chemical Composition of AA 2024-T3

Chemical Composition (wt %)							
Cu	Mg	Si	Fe	Cr	Zn	Mn	Al
3.80-4.90	1.20-1.80	0.00-0.50	0.00-0.50	0.00-0.10	0.00-0.25	0.30-0.90	bal.

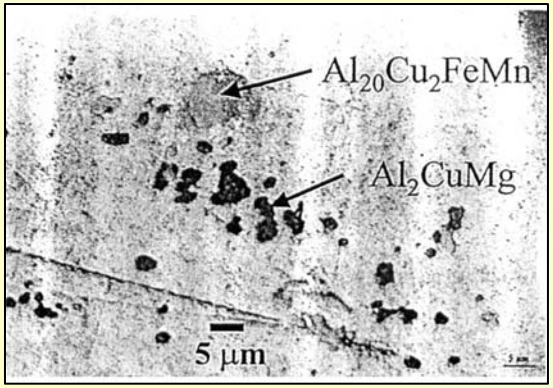
Adition of Cu, Mg, Zn and Fe (intermetallic) → Better mechanical properties (when compared with aluminum)

Lower corrosion resistance

Chemical Composition and Potential of Intermetallics

Phase	Atomic composition (%)[1]					Potential[2] mV vs ESC
	Al	Mg	Cu	Mn	Fe	
$Al_{20}Cu_2(MnFe)_3$	71.43	---	7.14	10.71	10.71	-675
Al_2CuMg	49.28	26.06	24.66	---	---	-920
Al_2Cu	66.69	---	33.31	---	---	> -880
Al (matrix)	---	---	---	---	---	-880

(1) *In* G. O. Ilevbare e J. R. Scully, *Corr. Sci.*, 53, p.134 (2001)
(2) *In* R.G.Bucheit, *J. Electrochem. Soc.*, 142, p.3994 (1995)



Optical image of AA2024-T3 after polish. Identification of intermetallic particles based on EDS

In W. R. McGovern, P. Schmutz and al, *J. Electrochem. Soc,*147, p.4494 (2000)

Why is Chromium so Extensively Used?

➔High efficiency and low cost
-Prevents corrosion
-Adhesion promoter for organic coatings and adhesives.

➔ Reliable: The process has low sensitivity towards variation in process conditions.

➔Effective on several metals and alloys.

➔Quality control: It is possible to know the amount of chromium on the surface by the color of the conversion coating.

- Toxic
- Classified as human carcinogen
- Workers at the production line are concerned about their health – liability for claims of workspace exposure
- Consumers are concerned about hexavalent chromium present in products
- Concern about hexavalent chromium in the environment, e.g. drinking water
- Treatment of waste
  - Stringent disposal limits

Alternatives to Chromium

- ➔ Redox reaction with precipitation
  - Molybdenum
  - Manganese
- ➔ pH controlled precipitation
  - Phosphate
  - Titanium/zirconium - based processes
  - **Rare earth salts**
  - Trivalent chromium
- ➔ Coupling agents between aluminium oxide and paint
  - **Silanisation (silanes)**
  - Siloxanes (sol-gel coating)
  - Polymerization
- ➔ Strengthening the aluminium oxide (anodizing)

SILANES → Hybrid compounds that can be used as coupling agents at the inorganic / organic interface

Mono-Silanes $X_3Si(CH_2)_nY$

where:
Y= organo-functional group: e.g., vinyl (-HC=CH2), amino (-NH2) or mercapto (-SH)
X=hydrolysable alkoxy group: e.g., methoxy (OCH_3) or ethoxy (OC_2H_5)

Bis-Silanes $X_3Si(CH_2)_nY(CH_2)_nSiX_3$

(The functional group Y can be for example an amine group or a chain of sulphur atoms)

Silanes

- **Mono-silanes** $X_3Si(CH_2)_nY$

EX:

vinyltriethoxysilane (VS, $CH_2CHSi(OC_2H_5)_3$),

γ-mercaptopropyltrimethoxysilane (γ-MPS, $SH(CH_2)_3Si(OCH_3)_3$,

γ-ureidopropyltriethoxysilane(γ-UPS, $H_2NCONH(CH_2)_3Si(OC_2H_5)_3$)

Bis-silanes $X_3Si(CH_2)_nY(CH_2)_nSiX_3$

EX:

Non-functional bis-silane:

bis-1,2-[triethoxysilyl]ethane (BTSE)

$(C_2H_5O)_3Si\text{-}(CH_2)_2\text{-}Si(OC_2H_5)_3)$

Functional bis-silane:

bis-[triethoxysilylpropyl]tetrasulfide **(BTESPT)**

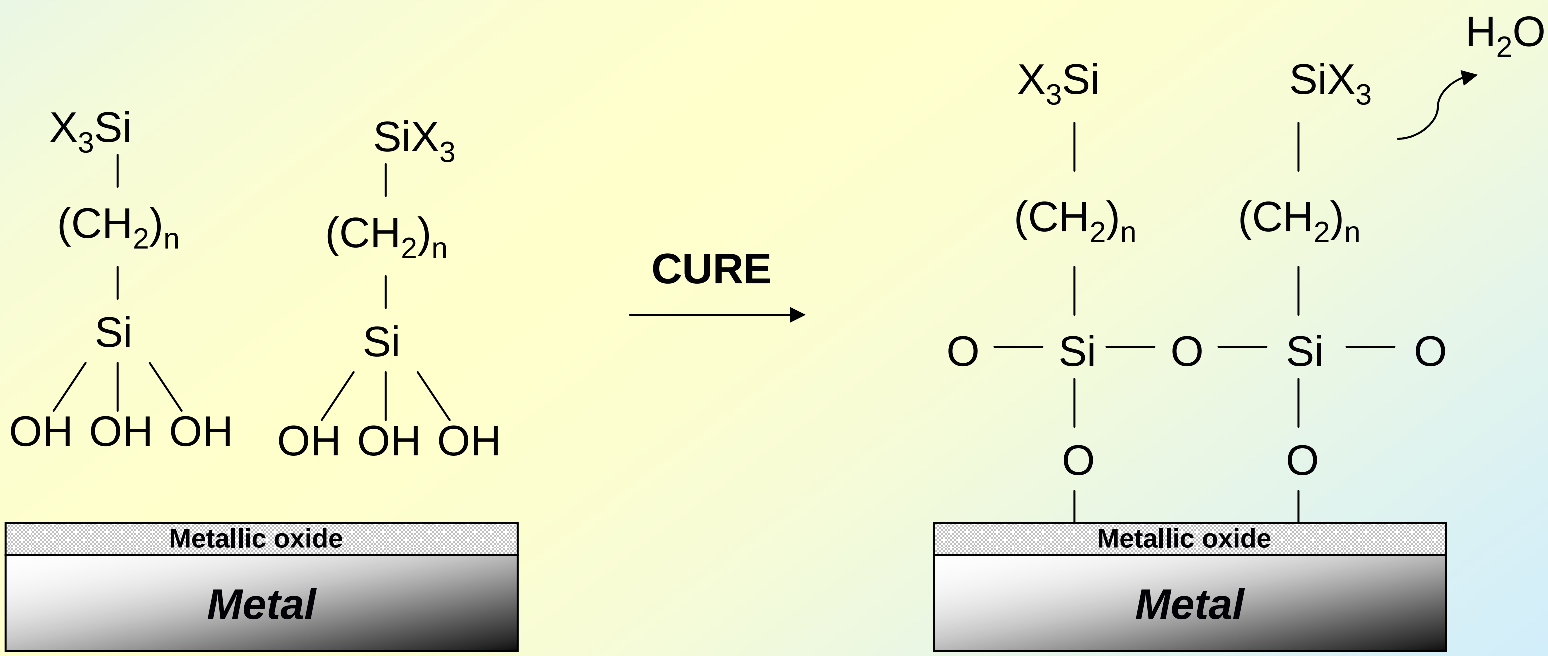
$(C_2H_5O)_3Si\text{-}(CH_2)_3\text{-}S_x\text{-}(CH_2)_3\text{-}Si(OC_2H_5)_3)$

Mechanism of Coating Formation with Silanes

1st Step - HYDROLYSIS

$$X_3Si(CH_2)_nSi(OCH_3)_3 \longleftrightarrow X_3Si(CH_2)_nSi(OH)_3 + 3CH_3OH$$

2nd Step – BINDING TO THE SUBSTRATE



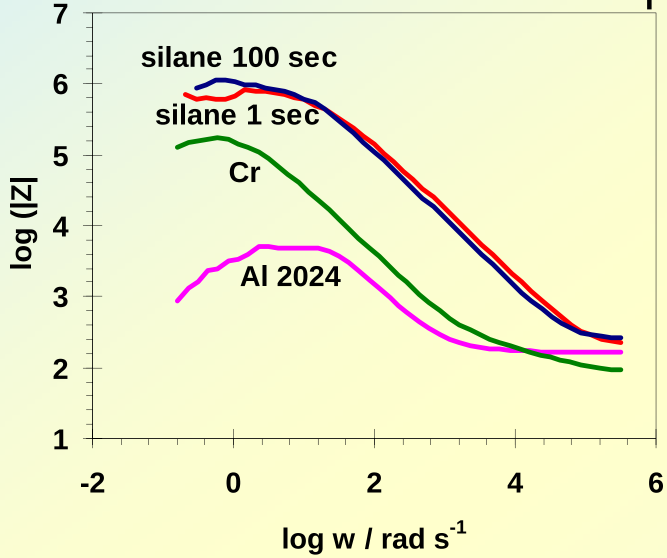
EIS Results – Immersion in a 0.1M NaCl

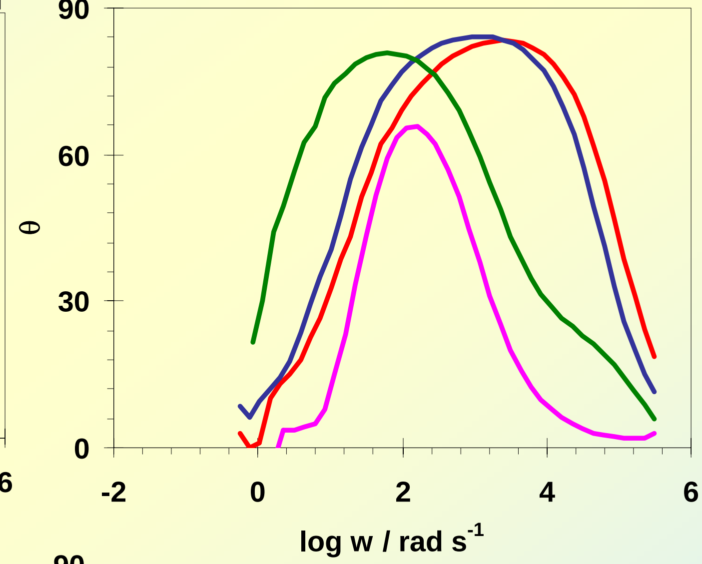
AA 2024-T3 pre-treated with BTESPT 4%

10 minutes of immersion

Impedance for silane is about one order of magnitude higher than that of Cr

One time constant at high frequencies due to the silane film



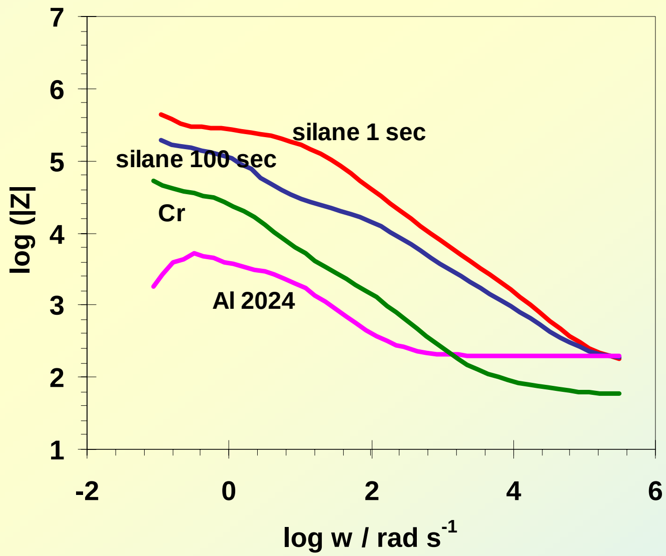


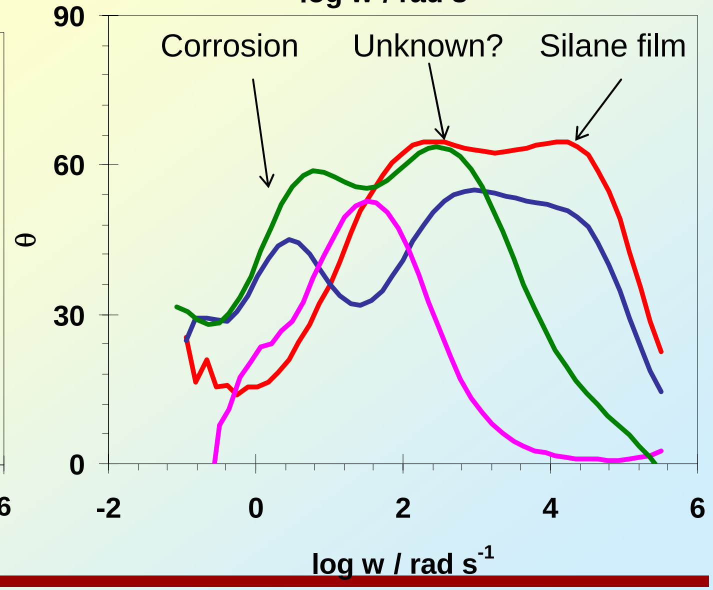
24 hours of immersion

Impedance decreases but is still higher for silanes.

A new time constant appears on the spectra

Unknown phase with S?





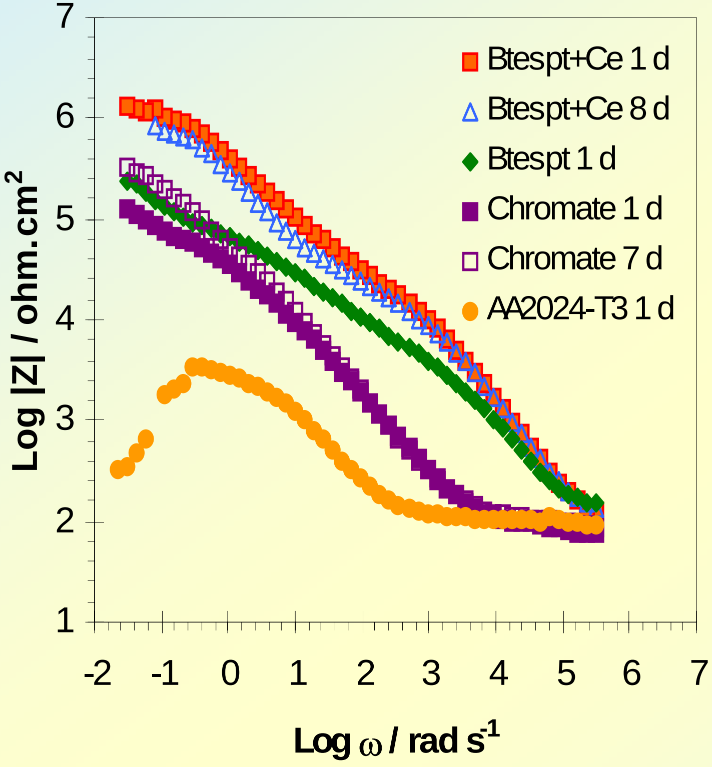
Combine the barrier properties of silane coatings with the inhibiting properties of Ce ions.

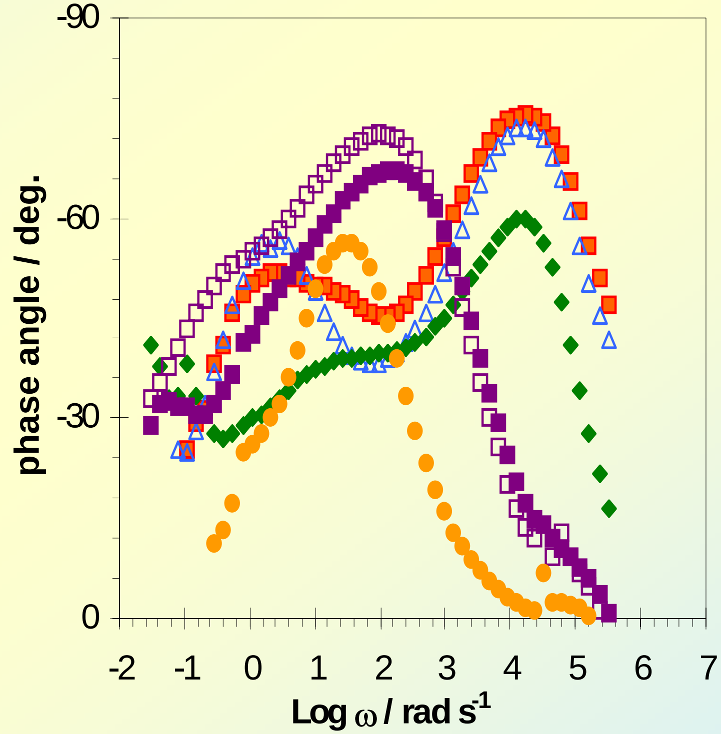
Silane doped solution

BTESPT in methanol **mixed with an aqueous solution of $1x10^{-3}$ M $Ce(NO_3)_3.6H_2O$ (5.5 % vol/vol).**

Doped Silane films - EIS results

AA2024-T3 substrates, pre-treated with different solutions.
Immersion in 0.1M NaCl



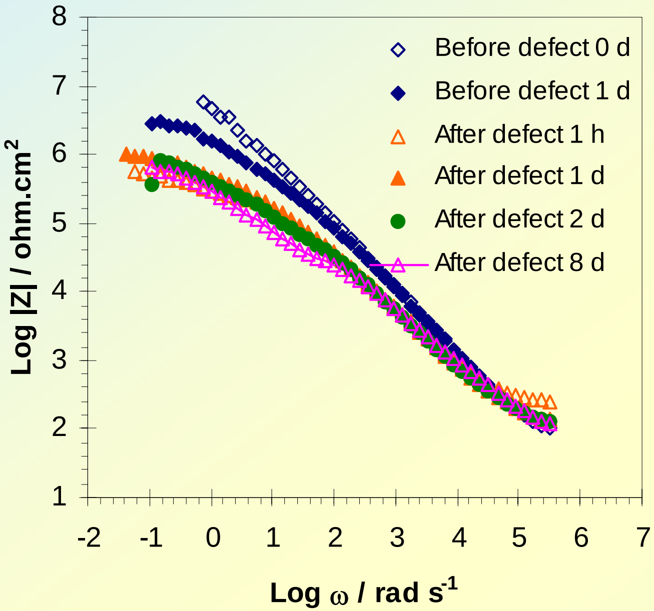


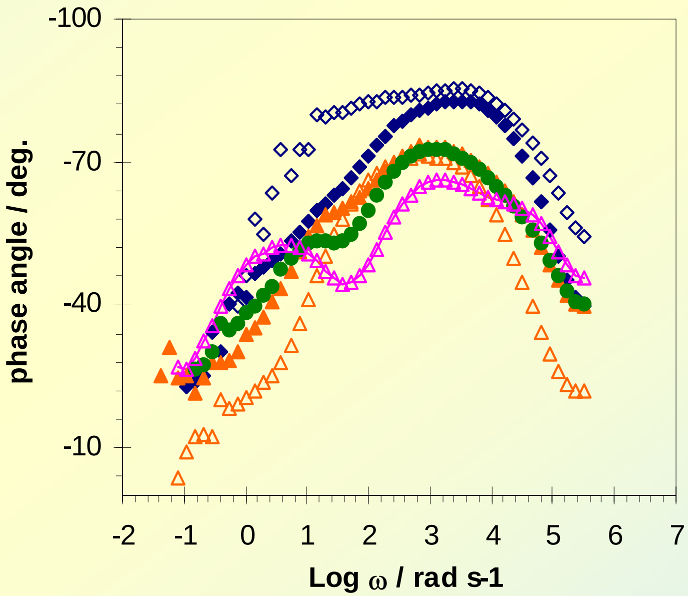
Impedance values of the doped film are higher than those obtained with the other pre-treatments.

Doped Silane films - EIS results

AA2024-T3 substrate, pre-treated with BTESPT doped with $Ce(NO_3)_3$.

After 24h of immersion in 0.1 M NaCl a defect was artificially created on the surface.





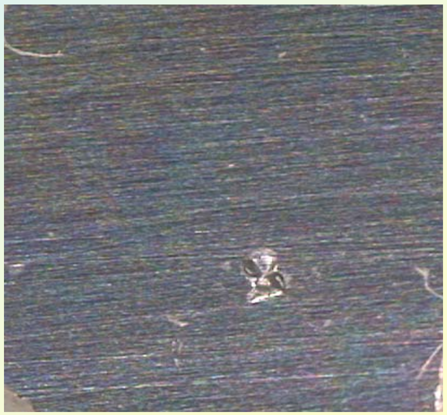
After the creation of the defect a small decrease of the impedance values and some dispersion in the low frequency range reveals corrosion onset.

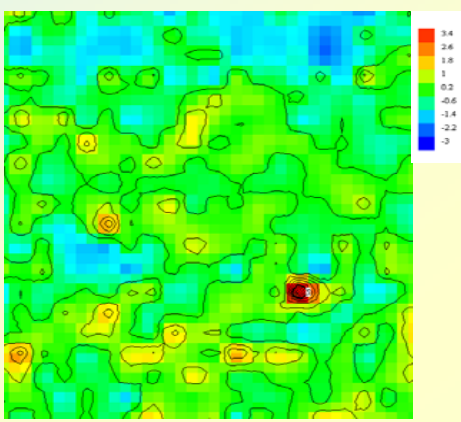
24 h after defect formation the impedance remains approximately constant revealing that corrosion could not proceed. The same trend was observed after one week of immersion.

This results shows that the doped film possesses corrosion inhibiting properties.

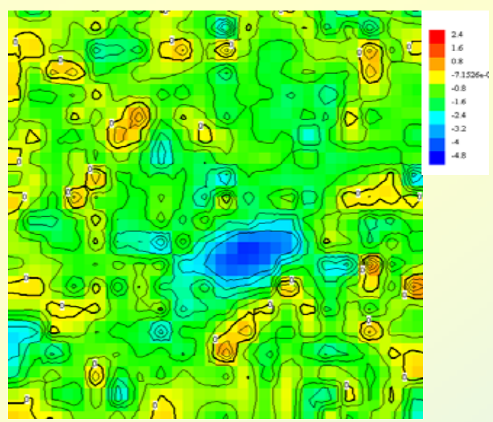
Effect of Cerium Nitrate Addition

AA2024-T3 pre-treated with BTESPT doped with Cerium nitrate (10-3 M)
Immersion 24 h before the formation of a defect





10 min after defect



24 h after defect

Reduced anodic activity was observed 10 min after defect formation.

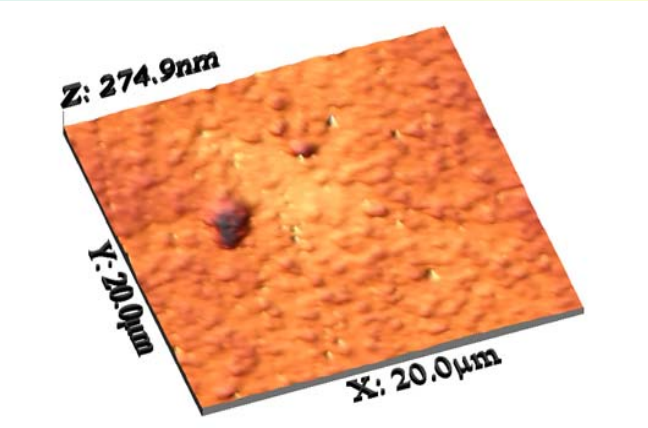
The cerium ions entrapped in the silane film can move to the corrosion area and form hydroxide precipitates on top of cathodic intermetallic particles due to the enhanced pH and presence of H_2O_2 in such areas

The precipitates blocks the cathodic zones suppressing the corrosion activity of defects.

Scanned area: 2 mm x 2 mm. Scale units: µA cm^2.

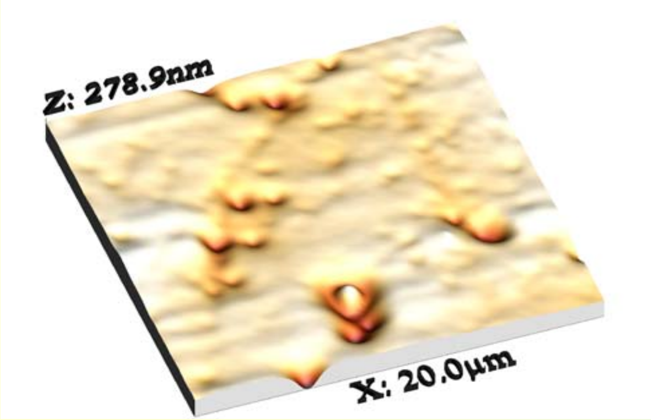
AFM results

Ce-doped coating on AA2024-T30



The **doped film** presents an oxide type structure with some particles and pores in the outer layers.

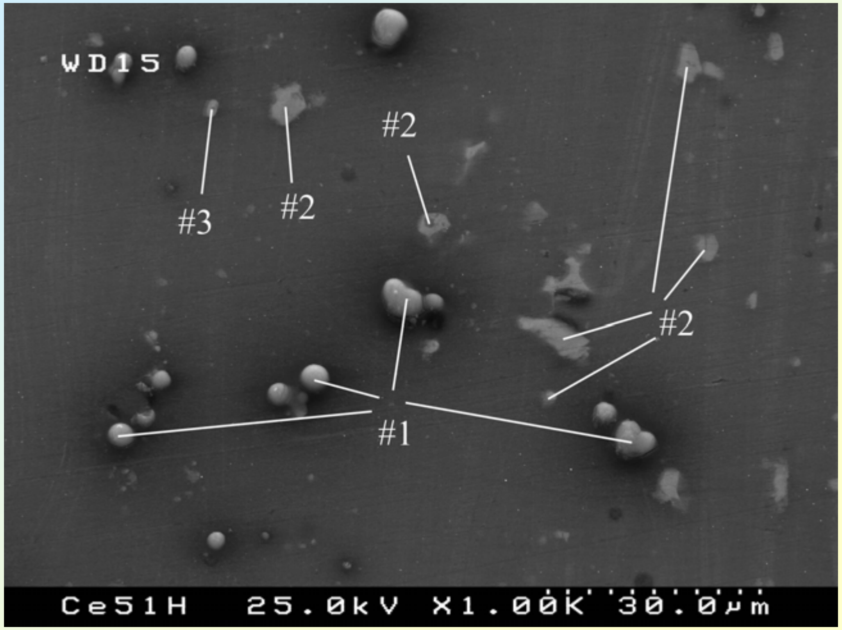
No doped coatings on AA2024-T3

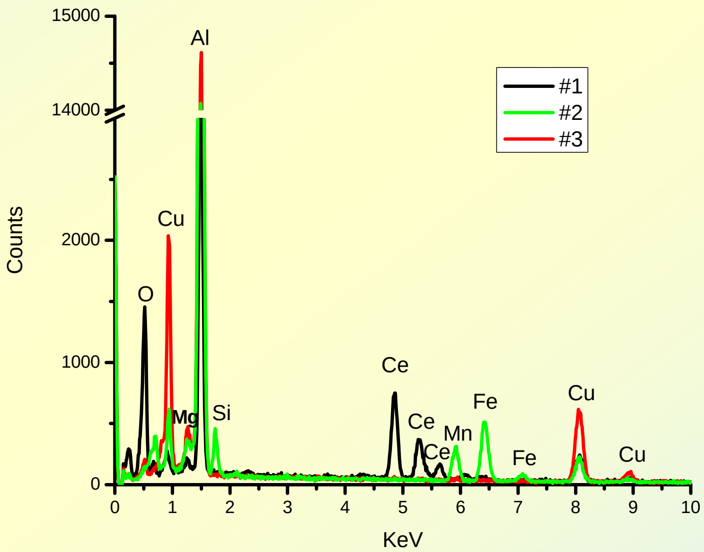


The **no doped** film is more heterogeneous and porous, presenting lower thickness (the topography of the coated alloy repeats in several places the topography of polished alloy).

Cerium ions not only confer "self-healing" effect but also lead to formation of thicker film probably due to the influence on silane polymerisation processes

SEM / EDS results



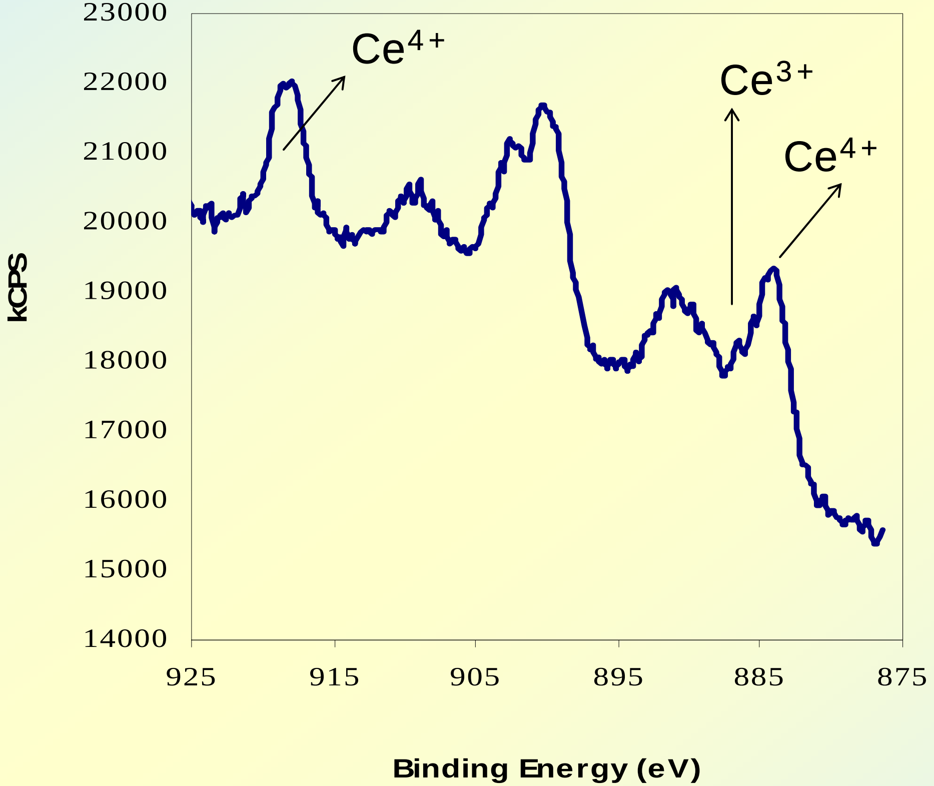


SEM image (a) with EDS spectra in different places of surface (b) of the AA2024 after immersion for 1h in 0.005M NaCl doped with $Ce(NO_3)_3$

Deposition of cerium hydroxide occurs preferably at the zones of very active S-phase intermetallics

XPS results

AA2024 pre-treated with BTESPT after 9 days of immersion in 0.1 M NaCl containing $5.5x10^{-5}$ M $Ce(NO_3)_3$



The surface film is composed by a mixture of Ce^{3+} and Ce^{4+} with predominance of Ce^{4+}, probably CeO_2.

The corrosion inhibition process involves oxidation of Ce^{3+} to Ce^{4+}

Conclusions

•Pre-treatments using bis-[triethoxysilylpropyl] tetrasulfide silane **doped** with small amounts of cerium nitrate seems to have a promising future as chromate replacers for AA 2024-T3.

•During the early stages of immersion the corrosion protection is provided by a surface coating with low porosity containing Ce^{3+} and Ce^{4+} species.

•The long-term protection is likely to result from the “self-healing” properties of the Ce ions. In fact, even for aggressive solutions corrosion did not proceed in aluminium substrates.

Acknowledgements

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