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Multiple action self-healing coatings for Active Corrosion Protection of Metals

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VUB - TU-Delft*

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Research consortium

VUB:

- For polymer science: Guy Van Assche, Bruno Van Mele
- For surface engineering&characterisation: Iris De Graeve, Herman Terryn
- Students: Gill Scheltjens, Thibault Muselle, Joost Brancart

Close collaboration with TU-Delft:

- For local electrochemical techniques: Arjan Mol, Yaiza Gonzalez Garcia
- For self-healing and inhibitor experience: Santiago Garcia

⇒ Exchange of experience, research tools & methodology

⇒ Focus on different types of self-healing systems, concepts

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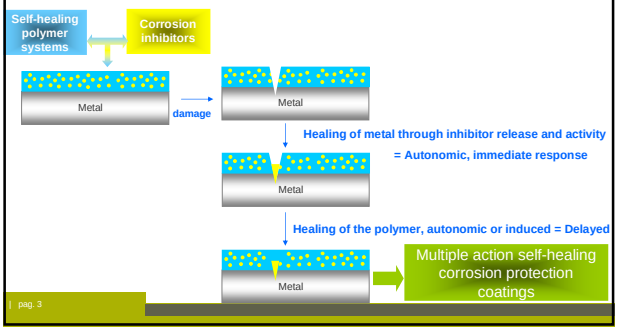
Concept of multiple action self-healing polymer coating



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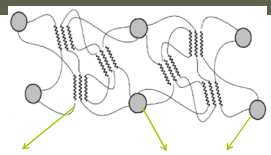
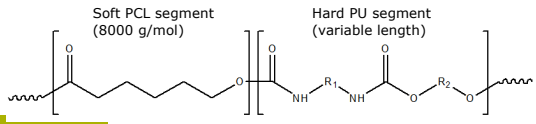
Self-healing based on "shape memory polymer" concept

- PCL/PU block copolymer
- Physical network
  - Soft PCL matrix
  - Hard PU segments
    - 12, 30 & 41 wt%
    - 0, 5, 8, 12 & 16 wt%



Soft matrix
$T_{m,PCL}$ = 52°C < $T_{healing}$ <$T_{m,PU}$ = 173°C
Hard phases



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Coating ingredients & application method

- **Substrate:** Aluminum 99,99 % and AA2024 (activated in NaOH solution)
- **Inhibitor**: Cerium(III) nitrate hexahydrate; $Ce(NO_3)_3 \cdot 6H_2O$
- **Polymer coating preparation**:
  - Concentration of SMPU without/with inhibitor
  - Temperature = 80 ℃
  - Bar coating at 80 ℃ >>> 1-3 µm layer

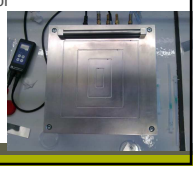

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Illustration of methodology

- Polymer healing action
  - Local healing: Hot stage Atomic Force Microscopy
  - Macroscopic: Electrochemical Impedance Spectroscopy
- Inhibitor action
  - X-ray Photoelectron Spectroscopy
  - Scanning Vibrating Electrode Technique (TU Delft)
  - Scanning Electrochemical Microscope (TU Delft)
- Multiple action
  - Electrochemical Impedance Spectroscopy

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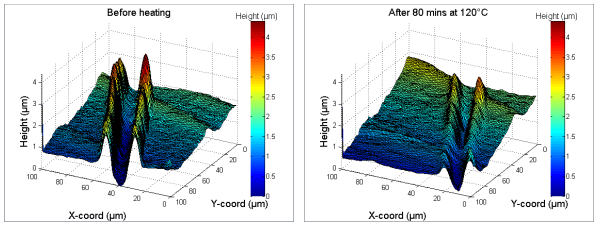
Polymer healing action
AFM on PU 12% coating



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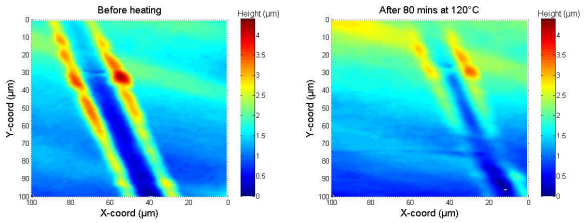
Polymer healing action
AFM on PU 12% coating



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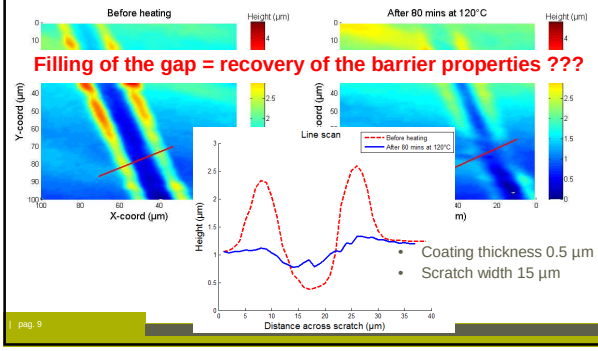
Polymer healing action
AFM on PU 12% coating



Filling of the gap = recovery of the barrier properties ???

- Coating thickness 0.5 µm
- Scratch width 15 µm

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Macroscopic polymer healing action
Electrochemical Impedance Spectroscopy

Principle:

Applied sinusoidal potential perturbation: $\tilde{U} = \Delta U \cdot \sin(\omega.t)$

(10 mV amplitude; freq 10 kHz-1 mHz)

>> Current response is also sinusoidal: $\tilde{I} = \Delta I \cdot \sin(\omega.t + \phi)$

>>> Impedance (Z): $Z(\omega) = \frac{\tilde{U}}{\tilde{I}} = |Z| \cdot \exp(i \cdot \phi)$

Frequency dependent | Amplitude | Phase angle ⇨ **Bode plots**

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Macroscopic polymer healing action
EIS

Experimental procedure: (1) Initial impedance of undamaged coating

(2) Impedance after application of a macroscopic scratch

(3) Impedance after thermal treatment for induced healing

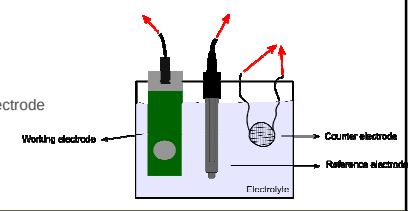
3 electrode setup:

WE = coated AA2024

RE = Ag/AgCl reference electrode

CE = Platinum mesh

Electrolyte = 0.1 M Na_2SO_4



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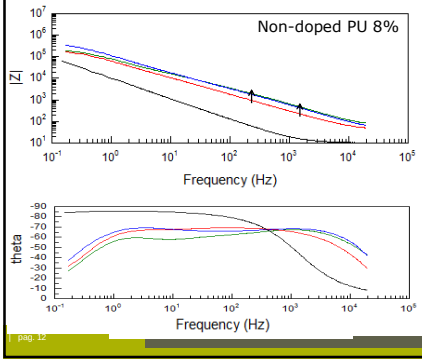
Macroscopic polymer healing action
EIS on non-doped coating



Black: Al substrate
Green: Initial coating
Red: Scratched coating
Blue: Healed coating

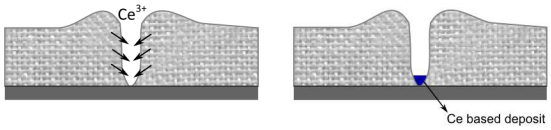
>> Recovery of barrier properties

Cerium action

- Precipitation on cathodic sites
  - Increase of pH
  - Precipitates:

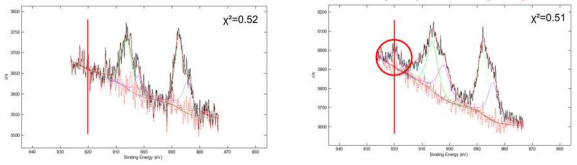
$$Ce^{3+} + 3\,OH^- \rightarrow Ce(OH)_3\downarrow$$

$$Ce(OH)_3 + H_2O \rightarrow CeO_2\downarrow + \ldots$$



Cerium action
X-ray Photoelectron Spectroscopy of cerium-doped coating on AA2024

Ce(III) | Ce(III) & **Ce(IV)**



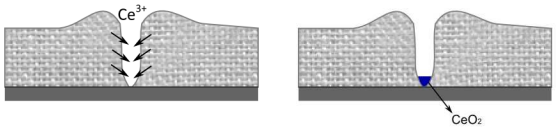
Non-damaged coating | 3 days after application of multiple scratches

$$Ce^{3+} + 3\,OH^- \xrightarrow{III} Ce(OH_3)\downarrow$$

$$Ce(OH_3) + H_2O \xrightarrow{IV} CeO_2\downarrow + \ldots$$

Cerium action
XPS

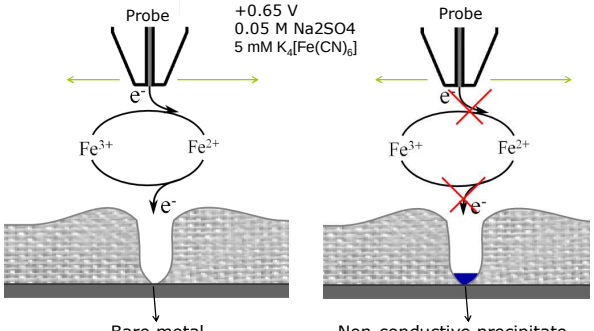
Ce(III) | Ce(III) & **Ce(IV)**



$$Ce^{3+} + 3\,OH^- \xrightarrow{III} Ce(OH_3)\downarrow$$

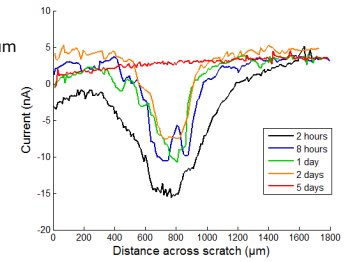
$$Ce(OH_3) + H_2O \xrightarrow{IV} CeO_2\downarrow + H^+ + e^-$$

Local cerium action
Scanning Electrochemical Microscopy



Local cerium action
SECM on Ce-doped scratched coating

Ce-doped
PU 12%
AA2024
Scratch ± 350 µm

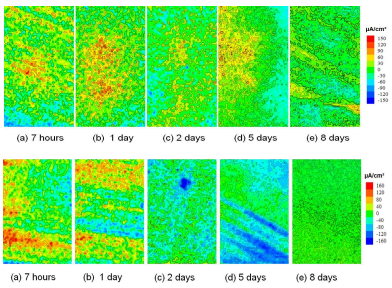


Courtesy of dr. Yaiza Gonzalez-Garcia (TU Delft)

Local cerium action
Scanning vibrating electrode technique

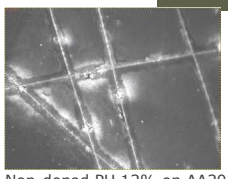
Non-doped PU 12% coating with scratch on AA2024 in 0.01 M NaCl

Ce-doped PU 12% coatingwith scratch on AA2024 in 0.01 M NaCl

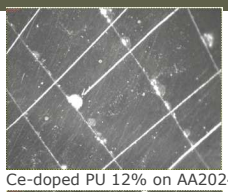


Courtesy of dr. Yaiza Gonzalez-Garcia (TU Delft)

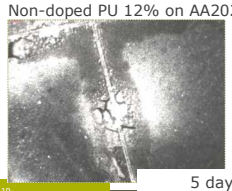
Cerium action
Optical microscope

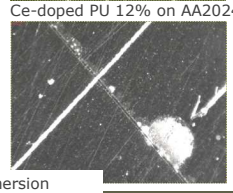


Non-doped PU 12% on AA2024



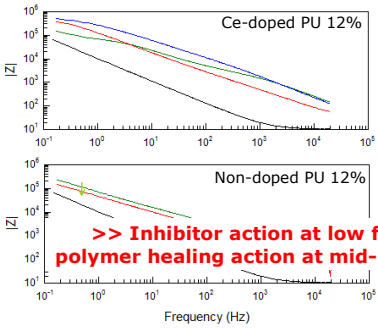
Ce-doped PU 12% on AA2024





5 days of submersion
(25 g/l Na_2SO_4 aqueous solution)

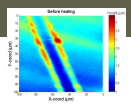
Multiple action self-healing
EIS

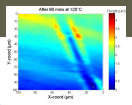


Black: Al substrate
Green: Initial coating
Red: Scratched coating
Blue: Healed coating

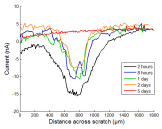
>> Inhibitor action at low frequencies + polymer healing action at mid-high frequencies

Conclusions

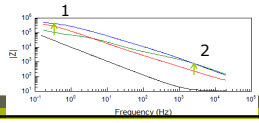




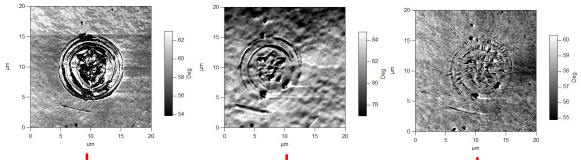
- Polymer healing action
  - Dependence wt% PU
- Cerium action
  - CeO_2 deposition in the scratch



- **Multiple-action self-healing**
  - **>>> Autonomous metal passivation**
  - **>>> Thermally induced recovery of barrier properties**



Proof of concept demonstrated on VUB logo



Top view of SMPU coating, locally 'damaged' with VUB logo using nano-lithographic AFM tip

during heating to 80 ℃
>> flow of soft phases
>> fading of the contours

after healing procedure
>> stitching of the logo
>>> healing of damage!