New Zinc-Based Automotive Steel Protection Technologies – Coated Steel Performance

ZCO-45-7

T. Prosek

GAP Meeting, 05/06/2015
Background

• Significant efforts invested into development of new zinc-based coatings during past decades
• Number of innovative coating compositions available
• Market share of alloyed zinc-based coated steel products seems to grow steadily
• ZCO-45 programme of GAP: Can any other element enhance corrosion stability of zinc coatings?
Project ZCO-45-6

- Model cast alloys Zn-X, Zn-5Al-X, Zn-6Mg-X and Zn-3Al-2Mg-X, \( X = \) Ti, Ce (mischmetal), Zr, Mo, Cr, B, Ga, In, Cu, Ni, Ca, Mn and Si: 69 comp.

- Microstructure, hardness and galvanic protection ability evaluated, but main focus on corrosion stability:
  - Accelerated lab testing – open configuration
  - Accelerated lab testing – confined zones
  - Surface activity
  - Field exposure at a marine site \( \text{New 2-year data} \)
Lab tests: Open configuration

- Quaternary Zn-Al-Mg-X alloys most stable
- It is advantageous to combine Al and Mg
- Small additions of Ce (Mm), Cr, Si, Mn, Mo, Ti, Zr can increase corrosion stability, mostly at lower concentrations 0.2–0.6 wt.%
- Good galvanic protection
Lab tests: Confined zones

- Corrosion in confined zones often critical for car bodies

**ECC1**

**6 weeks**

P H range
crevice: 4–5
to 10–12
(open: 8–9)

Corrosion accelerated in crevice due to separation of anodic and cathodic sites
Summary confined / open

- Effect of alloying elements different in open and crevice configuration

<table>
<thead>
<tr>
<th>Element</th>
<th>Open</th>
<th>Crevice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Positive</td>
<td>Negative</td>
</tr>
<tr>
<td>Mg</td>
<td>Positive</td>
<td>Strongly positive without Al, mostly neutral with Al</td>
</tr>
<tr>
<td>Cr</td>
<td>Slightly positive</td>
<td>Positive to neutral</td>
</tr>
<tr>
<td>Mm (Ce)</td>
<td>Positive to slightly negative</td>
<td>Neutral</td>
</tr>
<tr>
<td>Ti</td>
<td>Slightly positive</td>
<td>Positive with Al, neutral with Al and Mg</td>
</tr>
<tr>
<td>Ca</td>
<td>Slightly negative</td>
<td>Slightly positive to neutral</td>
</tr>
<tr>
<td>Mn</td>
<td>Slightly positive</td>
<td>Slightly positive</td>
</tr>
<tr>
<td>Si</td>
<td>Positive</td>
<td>Positive from 0.6%</td>
</tr>
<tr>
<td>Zr</td>
<td>Positive</td>
<td>Neutral</td>
</tr>
</tbody>
</table>

Positive = Inhibition of corrosion; Negative = Increase in mass loss

Inhibiting effect in both open and crevice:
Mg > Si >> Cr > Mn
Field exposure

- **Marine site** in Brest, France: C5 for steel, 12°C, 81% RH, Cl⁻ deposition 3.5 g/m² day, pH 5.6, rain 99 mm/month, ToW 448 h/month
- Four samples of selected alloys fixed on plastic support + reference panels, 45° south
- Mass loss measured after 10 and 24 months
Field exposure: 24 months

Huge difference between cast Zn and HDG
Strong synergy Al / Mg
Field 24M vs. ECC1

Zn-Mg(-X): Worse outdoors; Zn-Al-Mg(-X): Better outdoors
Al important for long-term stability, Mg initially
Field exposure: Appearance

10M Zn 24M 10M Zn-5Al 24M

10M Zn-3Al-2Mg 24M 10M Zn-3Al-2Mg-0.5Cr 24M
Field exposure: Zn-Al-Mg-X

- **Cr**: Somewhat efficient in binary and ternary alloys, no improvement in Zn-3Al-2Mg
- **Zr**: No improvement in Zn-3Al-2Mg, efficient in Zn-Zr and possibly in Zn-Mg-Zr
- **Ti**: Effect unclear
- **Si**: Possible inhibition, large difference between samples
- **Mm (Ce)**: Possible inhibition up to 0.6 wt.%
- **Mo**: Mass loss non-measurable
- **Mn**: Good results at all concentrations
Objectives of ZCO-45-7

• Materials with good performance identified; due to the importance of microstructure, the study needs to pursue with coatings

• To apply the most promising Zn-Al-Mg-X compositions as steel coatings

• To assess their corrosion stability as well as selected other properties of interest for automotive applications
Sample preparation

- Hot dipping using simulator: McMaster University
- Substrate: IF full hard 0.8 mm thick steel
- 16 to 20 panels of at least 100×100 mm per composition
- Coating thickness target: 7 µm

\[
\text{N}_2 + 5\% \text{H}_2 \quad \text{d.p.} -30 \, ^\circ\text{C}
\]

\[
\begin{align*}
720 \, ^\circ\text{C}, & \quad 60 \, \text{s} \\
460 \, ^\circ\text{C}, & \quad 15 \, \text{s} \\
\text{Zn bath}, & \quad 5 \, \text{s} \\
\end{align*}
\]

\[
\begin{align*}
10 \, ^\circ\text{C/s} & \quad 0 \, \text{s} \\
20 \, ^\circ\text{C/s} & \quad 100 \, \text{s} \\
20 \, ^\circ\text{C/s} & \quad 200 \, \text{s}
\end{align*}
\]
### Material selection

- **Priority list** based on ZCO-45-6 results

<table>
<thead>
<tr>
<th>Material</th>
<th>Improvement to Zn</th>
<th>Galvanic protection</th>
<th>Hardness HV₅</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Open, lab</td>
<td>Open, field</td>
<td>Crevice, lab</td>
<td></td>
</tr>
<tr>
<td>Zn-3Al-2Mg-2Si</td>
<td>80%</td>
<td>81%</td>
<td>79%</td>
<td>Superior</td>
</tr>
<tr>
<td>Zn-3Al-2Mg-0.5Cr</td>
<td>79%</td>
<td>72%</td>
<td>78%</td>
<td>Superior</td>
</tr>
<tr>
<td>Zn-5Al-2Mg-2Si</td>
<td>85%</td>
<td>NA</td>
<td>99%</td>
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<tr>
<td>Zn-5Al-2Mg</td>
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<td>97%</td>
<td>Superior</td>
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<tr>
<td>Zn-3Al-2Mg-0.6Si</td>
<td>71%</td>
<td>NA</td>
<td>76%</td>
<td>Superior</td>
</tr>
<tr>
<td>Zn-3Al-2Mg-0.6Mn</td>
<td>51%</td>
<td>91%</td>
<td>64%</td>
<td>Good</td>
</tr>
<tr>
<td>Zn-3Al-2Mg-2Mn</td>
<td>63%</td>
<td>91%</td>
<td>40%</td>
<td>Good</td>
</tr>
<tr>
<td>Zn-3Al-2Mg-0.01Mo</td>
<td>74%</td>
<td>91%</td>
<td>15%</td>
<td>Good</td>
</tr>
<tr>
<td>Zn-3Al-2Mg-0.3Mn</td>
<td>63%</td>
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<td>59%</td>
<td>Good</td>
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**Green:** Top 15 materials; **Blue:** Good performance; **Red:** Performance similar to Zn; [1] Superior appearance after corrosion tests; [2] Toxicity of Cr(VI) / Ce(III) compounds; [3] Reference material

Excluded due to Ce(III) toxicity
Feasibility study (IC)

- Solubility of X in Zn-Al-Mg melt at 460 °C
- Different preparation paths tested: Direct, master alloys
- Non-stirred melt, argon protective atmosphere, holding time up to 1 week
- Composition verified on cast samples by XRF
Feasibility study: A-series

Zn-3Al-2Mg $\rightarrow$ Zn-3Al-2Mg-Mo

• Zn melt $\rightarrow$ Al added, 10 minutes $\rightarrow$ Mg added, 10 minutes; composition correct

  $\Rightarrow$ Zn-3Al-2Mg easy to prepare

(Al and Mg to be added in form of Zn-Al and Zn-Mg master alloys)

• Zn-3Al-2Mg melt $\rightarrow$ Mo powder packed in Al foil added, 24 hours: 0.01% Mo

  $\Rightarrow$ Zn-3Al-2Mg-Mo possible

(10-fold excess of Mo will be used to reach maximal possible concentration)
Feasibility study: B-series

Zn-3Al-2Mg-0.6Si → Zn-3Al-2Mg-2Si → Zn-5Al-2Mg-2Si

• Zn-3Al-2Mg melt → lump Si added, 24 hours: negligible solubility
• Zn-3Al-2Mg melt → AlSi40 master alloy added, 48 hours: negligible solubility; temperature increased to 550 °C, 1 week: 0.6% Si
• Zn melt → AlZn30Mg20Si20 master alloy added, 24 hours: 0.14% Si; 1 week: 0.7% Si

⇒ Zn-3Al-2Mg-0.6Si possible using AlZn30Mg20Si20 master alloy and long holding time
Feasibility study: B-series

Zn-3Al-2Mg-0.6Si → Zn-3Al-2Mg-2Si → Zn-5Al-2Mg-2Si

⇒ Zn-3Al-2Mg-2Si impossible
no procedure to get high Si content at 460 °C found

• Zn-3Al-2Mg-0.7Si melt → Al added, 1 hour: Al dissolved

⇒ Zn-5Al-2Mg-0.6Si instead of Zn-5Al-2Mg-2Si
Feasibility study: C-series

**Zn-3Al-2Mg-0.6Mn → Zn-3Al-2Mg-2Mn**

- **Zn-3Al-2Mg melt → Mn added, 24 hours:** negligible solubility
- **Zn-2Mg melt → AlMn40 master alloy added, 24 hours:** negligible solubility
- **Zn melt → AlZn30Mg20Mn20 master alloy added, 24 hours:** Zn-1.1Al-1.1Mg-0.3Mn obtained
- **Zn melt → Mn added, 48 hours:** 0.31% Mn instead of 2% Mn; 1 week: 0.6% Mn instead of 2% Mn
Feasibility study: C-series

\[ \text{Zn-3Al-2Mg-0.6Mn} \rightarrow \text{Zn-3Al-2Mg-2Mn} \]

- Zn melt, 100 g → 0.64 g Mn added, 1 week: Zn-0.46Mn → 2.1 g Mg + 3.2 g Al added: Zn-3.1Al-1.9Mg-0.4Mn → 1.5 g Mn added, 1 week: Zn-3.0Al-1.9Mg-0.46Mn

⇒ Zn-3Al-2Mg-0.6Mn possible
prepare Zn-Mn using surplus of Mn (1%), then Zn-Al and Zn-Mg

⇒ Zn-3Al-2Mg-2Mn impossible
slow dissolution kinetics, possible thermodynamic limitation
Feasibility study: D-series

Zn-3Al-2Mg-0.5Cr

- Zn melt → Cr powder packed in Al foil added, 24 hours: negligible dissolution
- Zn-3Al-2Mg melt → AlCr40 master alloy added, 24 hours: negligible dissolution; 1 week: 0.1% Cr
- Zn melt → AlZn30Mg20Cr5 master alloy added, 1 week: Zn-3.4Al-2.0Mg-0.05Cr

⇒ Zn-3Al-2Mg-0.5Cr impossible
   higher temperature needed

⇒ Zn-3Al-2Mg-0.1Cr possible
   Cr content lower but still considered interesting
   (0.2% Cr gave good results)
Feasibility study: E-series

Zn-3Al-2Mg-0.6Ti

- Zn melt $\rightarrow$ ZnTi5 master alloy added, 1 week $\rightarrow$ Al and Mg added, 24 hours: Zn-3.8Al-2.7Mg-0.4Ti $\Rightarrow$ Zn-3Al-2Mg-0.6Ti possible due to formation of insoluble phase $\text{Al}_x\text{Ti}_y$, Ti needs to be added in excess
### Feasibility study: Summary

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Green: Top 15 materials; Blue: Good performance; Red: Performance similar to Zn

- 7 materials pre-selected: Any more to add?
Substrate

- Laser cut IF full hard 0.8 mm thick steel from AM
- Light red rusting found: Reduced in N₂/H₂, but defects still visible
- Pickling in HCl, or new samples?
Timing, references, painting

- **Timing**: Series A in summer → Characterization → If OK, the rest (≈ end of year)

- **Reference materials:**
  - **HDG (GI)**: 7 µm (IF GI Z100 0.8mm supplied by AM), 20 µm in some tests (stock of IC)
  - **Zn-2Al-2Mg**: 7 µm, 20 µm in some tests (available at IC)
  - Others can be included in case of interest
Characterization

- Hardness
- Coating thickness and homogeneity: Cross-section analysis
- Chemical composition: x-ray fluorescence (XRF), ev. atomic absorption spectroscopy (AAS) after coating dissolution
- Phase composition: x-ray diffraction (XRD), light and electron microscopy (SEM / EDX)
Corrosion properties

• Several sub-tasks planned:

A. General corrosion stability (cosmetic corrosion) of non-painted panels
• N-VDA, 6 weeks and marine test site, 1 and 2 years
• Samples with masked edges
• Mass loss, surface appearance, corrosion depth

B. Protection against red rust formation in defects to steel on non-painted panels
• N-VDA, 6 weeks and marine test site, 1 and 2 years
• Exposed edges and scribe
• White and red rust formation around defects followed as function of time
Corrosion properties

C. Time to red rust appearance of formed panels

- N-VDA, duration depends on performance
- White and red rust formation assessed once a week in formed/non-formed areas until a threshold is reached (e.g., 10% of the area red rusted)
- Type of formed panels: Cups? Bend panels? Other?
D. Protection in defects of painted panels

• N-VDA, 6 weeks and marine test site, 1 and 2 years
• Automotive paint system to be applied in a line of Opel
• Scribe(s) and exposed cut edges, stone chipping
• Paint delamination from defects, red rust formation
Corrosion properties

E. Perforation corrosion study: Protection in confined zones simulating automotive hem flange configurations

- N-VDA, 6 weeks or longer
- Time to red rust formation, corrosion depth, remaining coating weight
- SEP 1160-1 panels with reduced size, preferably with glass window
Additional tests

• At least one panel per composition will be kept for an additional test to be selected based on results of the corrosion assessment

• Possible candidates:
  – Long-term corrosion stability
  – Temporary corrosion protection
  – Formability
  – Adhesive joining
  – Abrasion resistance
Mechanism

- Goal: Generalization, service life prediction
- 1 to 3 most promising materials, bare and painted
- **Identification of corrosion product** from field exposed samples by infrared spectroscopy (IR), ion chromatography (IC), x-ray diffraction spectroscopy (XRD), etc.
- **Electrochemical measurements** by electrochemical impedance spectroscopy (EIS), scanning Kelvin probe (SKP)
- **Specific lab experiments**
- Detail plan to be proposed later
Timing

• Started in November 2014

<table>
<thead>
<tr>
<th>Trimester</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
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<tr>
<td>Task 1 Material selection</td>
<td>–</td>
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<td>Task 2 Sample preparation</td>
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<td>Task 3 Material characterization</td>
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<td>Task 4 Corrosion properties</td>
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<td>Task 5 Additional tests</td>
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<tr>
<td>Task 6 Mechanism</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

• Year 1: Sample preparation and characterization
• Year 2: Corrosion testing
• Year 3: Specific tests, mechanistic study, evaluation of field exposed panels