Zagnelis™ - Zinc Aluminum Magnesium Coating for Automotive

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ArcelorMittal Global R&D
Outline

• Outline:
  • Zagnelis Product Development
  • Product & Process Description
  • Production Capabilities
  • Product Properties:
    − Forming, Tool Wear, Galling, Powdering/Cracking, & Stamping
  • Spot Welding
  • Adhesive Bonding
  • Corrosion & Corrosion Testing
    − Perforation, Cosmetic, Stone Chipping, Hybrid ZnAlMg/Al Assemblies
  • Outdoor/Natural Corrosion Testing
  • Conclusions
Product Development

• Product development timeline:
  - 2005 - ArcelorMittal initial lab work on ZnAlMg (ZM coatings)
  - Early 2008 – Optimal coating composition defined as: Zn, Mg 3.0%, Al 3.7% (wt %)
  - Sep 2008 – First line trial Mouzon (France)
  - Nov 2008 – Second line trial Eurogal (Belgium)
  - June 2010 – Commercial production begins @ Eurogal
  - 2nd Qtr 2012 – Commercial production begins @ Bregal (Germany)
Product & Process

- Coating composition: Zn, Mg 3.0%, Al 3.7% (wt %)

Hot Dip Galvanizing Process

Zn + Mg + Al  
ZnMgAl  
Steel  
Zagnelis – Surface Aspect
Production Capabilities

- Current product range – Available from Europe:

<table>
<thead>
<tr>
<th>Coating Designation</th>
<th>ZM70</th>
<th>ZM90</th>
<th>ZM120</th>
<th>ZM175</th>
<th>ZM195</th>
<th>ZM250</th>
<th>ZM310</th>
<th>ZM430</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating Mass (total both sides)</td>
<td>g/m²</td>
<td>70</td>
<td>90</td>
<td>120</td>
<td>175</td>
<td>195</td>
<td>250</td>
<td>310</td>
</tr>
<tr>
<td>oz/ft²</td>
<td>0.23</td>
<td>0.30</td>
<td>0.40</td>
<td>0.60</td>
<td>0.65</td>
<td>0.80</td>
<td>1.00</td>
<td>1.40</td>
</tr>
<tr>
<td>Coating Thickness (μm/per side)</td>
<td>5</td>
<td>7</td>
<td>10</td>
<td>14</td>
<td>16</td>
<td>20</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>Surface Treatment</td>
<td>C (E-Passivation® CrVI-free), O (oiled)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness</td>
<td>0.45 to 6.00 mm (0.018 to 0.236 inches)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Width</td>
<td>Up to 1680 mm (66 inches)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Production</td>
<td>Eurogal (Belgium) &amp; Bregal (Germany) Lines*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Note: Additional production sites under consideration
Potential Applications

• **Automotive:**
  - Doors – Hem flanges can be high corrosion areas
  - Deck Lids – Hem flanges & cut edge corrosion
  - Hoods – Stone chipping & hem flange corrosion
  - Body Sides – Cut edge corrosion & stone chipping
  - Fenders – Cut edge corrosion & stone chipping
  - Floor & Dash Panels – Difficult parts to form & corrosion
  - Structural & Reinforcement Parts – Cut edge & surface corrosion
Product Properties & Performance
• **Friction behavior versus GA:**

**FUCHS 4107S – Temp. 20 °C**
(mill oil)

- Zagnelis™ (ZnMgAl) coefficient of friction is generally lower than Galvanneal (GA) for a wide range of contact pressures and two oils
- Same trend is seen at higher temperatures (64°C)

**FUCHS 3802-39S – Temp. 20 °C**
(prelube)
Tool Wear

- Tool abrasion/wear results:

  Zagnelis™ tool wear similar to EG and HDG (GI) despite it’s a harder coating
  - It is less abrasive than GA and HDG + TOC (Thin Organic Coating)
  - No Zinc pickup (same as GA)
**Galling**

- **Coating aspect after 135 mm friction length**

  Strips lubricated one time with FUCHS 4107S

  ![Diagram showing Coatings with and without Stick-Slip](image)

  **Coatings - with Stick-Slip***

  - ElectroGalvanised
  - Galvanised
  - Galvannealed Iron 9%

  **Coatings without Stick-Slip***

  - Galvannealed Iron 12%
  - Galvannealed + L-Treatment
  - Electrogalvanised +PreP04
  - ZnMgAl

  * Note: Stick Slip is the spontaneous jerking motion & related noise that can occur when 2 objects are sliding over each other.
Galling

- Coating aspect after 2160 mm friction length

Strips lubricated one time with FUCHS 4107S

Coatings without Stick-Slip

- Overall Zagnelis (ZnMgAl) performs best with no Stick-Slip and minimal if any coating abrasion or scratches
Powdering/Cracking

- Powdering behavior

Oil: Lubrication FUCHS 4107S applied in excess

- Zagnelis™ has low powdering values which are similar to GI & EG, and much lower than GA
Stamping behavior

Oil: FUCHS4107S

- Zagnelis™ coatings allow the use of higher blank hold down forces than reference Zn coatings. Blank holder force can be similar to Zn coatings with the use of surface treatments.

* Note: Beta is the ratio between blank diameter before stamping and punch diameter.
Spot Welding

• Spot welding range & electrode life (ZM70 & Z100):

<table>
<thead>
<tr>
<th>Standard</th>
<th>PUDF 0.65 – 0.74 mm</th>
<th>PUDF 0.75 – 0.84 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating</td>
<td>GI Z100</td>
<td>ZM70</td>
</tr>
<tr>
<td>Steel thickness [mm]</td>
<td>0.74</td>
<td>0.80</td>
</tr>
<tr>
<td>Current [Hz]</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Welding time [periods]</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Holding time [periods]</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Welding force [daN]</td>
<td>210</td>
<td>230</td>
</tr>
<tr>
<td>Holding force [daN]</td>
<td>210</td>
<td>230</td>
</tr>
<tr>
<td>Electrode type</td>
<td>F16 – 5.5mm</td>
<td>F16 – 5.5mm</td>
</tr>
<tr>
<td>Min. avg. plug diameter [mm]</td>
<td>$4\sqrt{t}=3.44$</td>
<td>$4\sqrt{t}=3.57$</td>
</tr>
</tbody>
</table>

Weld Current Range

Electrode Life

<table>
<thead>
<tr>
<th></th>
<th>Z100</th>
<th>ZM70</th>
</tr>
</thead>
<tbody>
<tr>
<td># of Spot Welds</td>
<td>~465</td>
<td>~465</td>
</tr>
</tbody>
</table>

• Slightly larger current range for 0.74 mm GI Z100 (7 µm) vs. 0.80 mm ZM70 (5.5 µm)
• Similar electrode life for Z100 & ZM70
Spot Welding

• Spot welding range & electrode life (ZM70-140):

<table>
<thead>
<tr>
<th>SEP1220-2 Standard (PUDF)</th>
<th>ZM70</th>
<th>ZM100</th>
<th>ZM140</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steel thickness [mm]</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current [Hz]</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Welding time [periods]</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Holding time [periods]</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Welding force [daN]</td>
<td>230</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Holding force [daN]</td>
<td>230</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
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<td>$4\sqrt{t}=3.57$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Weld Current Range</th>
<th>ZM70</th>
<th>ZM100</th>
<th>ZM140</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current (kA)</td>
<td>1.1 kA</td>
<td>1.2 kA</td>
<td>1.1 kA</td>
</tr>
</tbody>
</table>

• No difference between ZM70 (5.5 µm), 100 (8 µm), & ZM 140 (11 µm) weld current range
• Longest electrode life with ZM70
Adhesive Bonding

- **Influence of Mg and Al content:**

<table>
<thead>
<tr>
<th>ZnAlMg Compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Al</td>
</tr>
<tr>
<td>1.5</td>
</tr>
<tr>
<td>17.8 ± 0.2</td>
</tr>
<tr>
<td>10%CF</td>
</tr>
<tr>
<td>90%AF</td>
</tr>
</tbody>
</table>

**Max stress (MPa)**

- **Failure Mode**

- Regardless of the magnesium & aluminum content, the failure mode is similar and primarily adhesive failure and an issue for all ZnAlMg coating compositions.
- Primarily Mg & Al surface oxides, MgOx probably contribute to adhesive failure.
- Note: CF = Cohesive Failure (good), AF = Adhesive Failure (bad).
Adhesive Bonding

• Crash adhesive performance (initial Zagnelis data):

<table>
<thead>
<tr>
<th></th>
<th>Coating</th>
<th>Criteria</th>
<th>498</th>
<th>5089</th>
<th>5074</th>
<th>5076</th>
<th>1620</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max stress (MPa)</td>
<td>Zagnelis™ (ZM)</td>
<td>21.2</td>
<td>19.7</td>
<td>21</td>
<td>21.3</td>
<td>19.7</td>
<td></td>
</tr>
<tr>
<td>Failure locus (%)</td>
<td>Zagnelis™ (ZM)</td>
<td>60% CF</td>
<td>5% CF</td>
<td>90%CF</td>
<td>60% CF</td>
<td>5%CF</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>40%AF</td>
<td>95%AF</td>
<td>10%AD</td>
<td>40%AF</td>
<td>95%AF</td>
<td></td>
</tr>
<tr>
<td>Max stress (MPa)</td>
<td>GI (Z)</td>
<td>22.9</td>
<td>22.3</td>
<td>22.1</td>
<td>22.7</td>
<td>22.3</td>
<td></td>
</tr>
<tr>
<td>Failure locus (%)</td>
<td>GI (Z)</td>
<td>90%CF</td>
<td>80%CF</td>
<td>100% CF</td>
<td>100% CF</td>
<td>80%CF</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10%AF</td>
<td>20%AF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

0.8 mm ZM & Z

• Depending on the crash adhesive used, results can be from good to very bad.
• Generally ZM tends to fail at the steel-adhesive interface or very near to the surface when bonded with crash adhesives.
### Adhesive Bonding

**• Process improvement: Alkaline Activation**

<table>
<thead>
<tr>
<th>Coating</th>
<th>Criteria</th>
<th>1496V</th>
<th>5089</th>
<th>1630</th>
<th>498</th>
<th>492</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zagnelis™ (ZM) (ZM)</td>
<td>Max stress (MPa)</td>
<td>23.1</td>
<td>22.6</td>
<td>24.0</td>
<td>25.4</td>
<td>23.8</td>
</tr>
<tr>
<td>Failure locus (%)</td>
<td>100% CF</td>
<td>90%CF</td>
<td>100%CF</td>
<td>100% CF</td>
<td>100% CF</td>
<td></td>
</tr>
<tr>
<td>GI (Z)</td>
<td>Max stress (MPa)</td>
<td>21.0</td>
<td>21.4</td>
<td>22.1</td>
<td>23.8</td>
<td>23.6</td>
</tr>
<tr>
<td>Failure locus (%)</td>
<td>30%CF</td>
<td>50%CF</td>
<td>10% CF</td>
<td>85% CF</td>
<td>100%CF</td>
<td></td>
</tr>
<tr>
<td>70%AF</td>
<td>50%AF</td>
<td>90%AF</td>
<td>15%AF</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Max Stress Improvement (Zagnelis vs. GI)</td>
<td>10%</td>
<td>6%</td>
<td>9%</td>
<td>7%</td>
<td>1%</td>
<td></td>
</tr>
</tbody>
</table>

0.8 mm ZM & Z

- With Alkaline Activation, Zagnelis™ shows improved crash adhesive performance
- Other properties such as phosphate, paint behavior, or corrosion resistance are not affected
Accelerated & Outdoor Exposure Corrosion Performance
Automotive Corrosion

Types of Typical Vehicle Corrosion:

- Visible parts
  - Cosmetic corrosion
    - From scratches

- Hidden parts
  - Perforating corrosion
    - Door Flange cross section
  - Perforating corrosion (hollow zones)
  - Cut edge corrosion
  - Cut edges
Accelerated Corrosion

• Cosmetic Corrosion – Painted Panels – VDA621-415

Mean Delamination (mm) after 10 cycles (wks)

- GA slightly better than GI Z100 with ~equivalent thickness
- Zagnelis™ is the best coating based on cyclic corrosion criteria
Accelerated Corrosion

• Perforating Corrosion Tests on Full Panels
  VDA 621-415 / VDA 233-102 tests

Degreased samples, no phosphate treatment

- Zagnelis **maximum** corrosion depth 10 times less compared to GI (HDG)
- Zagnelis **mean** corrosion depth 30 times less compared to GI (HDG)
Accelerated Corrosion

- Perforating Corrosion Tests on Metal/Glass Assemblies
  VDA233-102 test

- Zagnelis has much less corrosion depth/pitting than GI (Z) and GA

Corrosion depth under glass flanges after 12 weeks

- Zagnelis has much less corrosion depth/pitting than GI (Z) and GA
# Accelerated Corrosion

## Stone Chipping Resistance with VDA Test:

Paint Delamination after Stone Chipping & 20 VDA621-415 Cycles

<table>
<thead>
<tr>
<th></th>
<th>GA 7µm</th>
<th>GI 10µm</th>
<th>Zagnelis™ 10µm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FLAT</strong></td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td><strong>DEFORMED</strong></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
</tbody>
</table>

- Zagnelis: Almost no degradation on corrosion resistance with deformation
- Zagnelis: Best stone chipped corrosion performance with & without deformation
Influence of Zagnelis (ZM) Coating Thickness with Al:

- Poor Aluminum corrosion (deep pitting) is observed with GI (Z) regardless of Zn coating thickness.
- For Zagnelis, ZM thickness affects Aluminum corrosion performance. ZM90 (7.5µm) is probably insufficient, while ZM120 (10µm) limits Al pitting up to ~12 VDA 233-102 cycles.
Bimetallic Corrosion

- VDA 233-102 Cycles Before Significant Aluminum Corrosion (pitting depth~100µm)

- Poor Aluminum corrosion results (~1 cycle or 7 days) are observed with GI (Z) regardless of Zn ctg. wt.
- Aluminum corrosion performance is significantly improved with Zagnelis (ZM250 or ZM120 vs. ZM90)
- Aluminum remains without any corrosion up to 20 cycles (140 days) when associated with ZM250
Bimetallic Corrosion

- Hybrid Flange Corrosion with Aluminum - GMW14872

68 Cycles
Underbody (UB), Exposure D 4 spray/cycle, method 1/2

- More corrosion products developed in Al combination with GI Z120 vs. ZM120
- Lower corrosion depths on Al when joined to ZM120 vs. GI Z120
Outdoor/Natural Exposure

- **GI (Z) & ZM Mass Loss after 2 & 3 Years:**

  ![Graph showing mass loss comparison between GI and ZM](image)

  - ZM appears to be the best coating in all environments - mass loss ~2 to 3 times less than GI
  - With chlorides - marine site Brest, France (BR) or without chlorides - rural Maizières, France (MZ) or urban East Chicago, IN (EC) sites
Outdoor/Natural Exposure

- **GI (Z) & ZM Cut Edge / Hole Corrosion after 5 years:**

  - GI (Z): Self-healing observed after 1 year, but protection only lasted 1 year.
  - ZM: Self-healing observed after 1 year, and continues to last at least 4 years.
  - ZM self-healing duration increased by a factor of 4 compared to GI.

  ![Diagram showing corrosion over time](Image)

  - Sample evaluation at Brest (France) - Seashore.

  ![Pictures after 5 years](Images)
### Outdoor/Natural Exposure

**Mobile Exposure on a Truck (in Europe):**

- Truck driven more than 150,000 km/year, (93,000 mi/yr) in various environments (road salts,...)

<table>
<thead>
<tr>
<th>Metal 1</th>
<th>Metal 2</th>
<th>Adhesive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gap width = 120 µm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Observation after 1 year - confined (test) area**

- Z140 – 10µm
- ZM120 – 10µm

- Sample observations after 1 year for perforating corrosion
- Almost no change on ZM samples while GI (Z) has red rust in confined (test) zone
Outdoor/Natural Exposure

- Mobile Exposure on a Truck (in Europe):

- Better corrosion performance of ZM vs. GI coatings in the field and confirm previously observations in lab accelerated corrosion tests

Max corrosion attack depths in confined (test) area after 4 years

- These results highlight the better performance of ZM vs. GI coatings in the field and confirm previously observations in lab accelerated corrosion tests

Unpainted open panels - Observation after 1 year

- Better corrosion performance of Zagnelis vs. GI. Truck results similar to static outdoor exposure in marine & non-marine environments
### Outdoor/Natural Exposure

- **Mobile Exposure on a Truck (in Europe):**

  *Cosmetic corrosion pictures after 2 years*

<table>
<thead>
<tr>
<th>Material</th>
<th>Scribe line width: 1 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZM120 (10µm)</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>Z140 (10 µm)</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
</tbody>
</table>

- **Much less blistering on ZM120 vs. GI Z140**
Conclusions

- Zagnelis (ZnAlMg) coatings have numerous opportunities/applications due to:
  - Press-shop performance
  - Increased durability and robustness
  - Improved corrosion protection
  - Hybrid corrosion protection
  - Potentially attractive alternative to batch galvanizing or post E-coating
Presentations will be available May 18 at www.autosteel.org

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