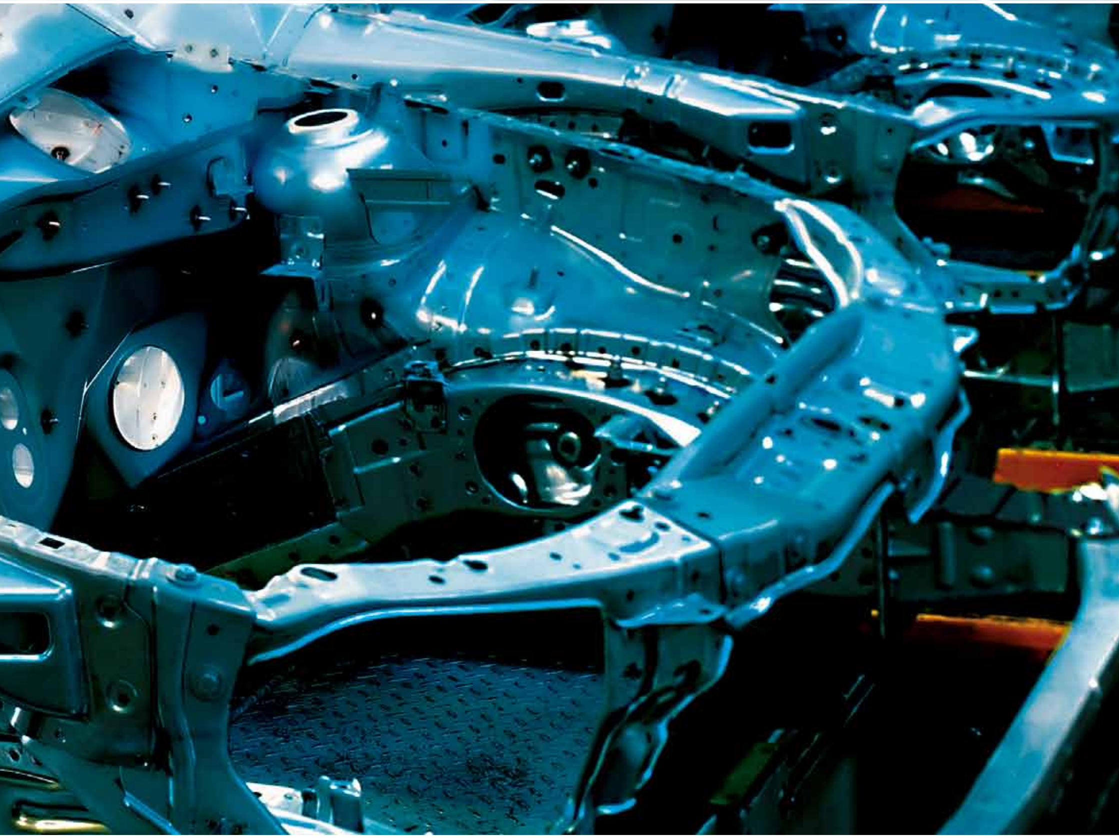
ZINC-MAGNESIUM-ALUMINIUM COATINGS FOR AUTOMOTIVE INDUSTRY



Steel Institute VDEh
at Stahl-Zentrum

Imprint

Publisher: Steel Institute VDEh, P.O. Box 105145, 40042 Duesseldorf

Phone: +49 211 6707-0, E-mail: info@vdeh.de, Internet: www.vdeh.de

Edited by Working Group "ZM coated product harmonization in Europe" of the Technical Committee Hot Dip Galvanised Strip at Steel Institute VDEh

All pictures were provided by the members of the Working Group.

First Edition 2013

Table of Contents

Introduction

Nearly two decades of experience with Zinc-Magnesium-Aluminium coatings (ZM) for Industry applications have proven the enhanced corrosion resistance of such coatings. Mechanisms leading to this improvement are well-known nowadays and described in the available literature.

During the 2000's, European steelmakers ArcelorMittal, Ruukki, Salzgitter, Tata Steel, ThyssenKrupp Steel Europe, voestalpine and Wuppermann all started adapting Zinc-Magnesium-Aluminium concepts to automotive applications.

While conducting, in most cases, their research separately, steelmakers nevertheless converged to form a unique new family of systems, including the same phases (Zn, $MgZn_2$, Al-rich Zn phase), Aluminium content* varying from 1.0 to 3.7 wt % and Magnesium content* from 1.0 to 3.0 wt %, i.e. the composition area of a metastable ternary diagram Zn-Mg-Al giving rise to primary Zinc and eutectic structure.

To help OEM figure out the potential of this new family of Zinc-Magnesium-Aluminium coatings, European steelmakers felt it more efficient to build a common technical communication. To achieve this objective, a working group was created at Steel Institute VDEh representing ArcelorMittal, Ruukki, Salzgitter, Tata Steel, ThyssenKrupp Steel Europe, voestalpine and Wuppermann. For more than one year, experts from those companies discussed tests and norms used to evaluate coatings behaviour and shared evaluations they had performed during the past few years. All properties of the European ZM coatings such as corrosion resistance, forming behaviour, joining and painting ability, were discussed, compared in detail and compiled in this publication. Z coatings were used as a reference.

Technical results shared, such as powdering or friction or galling demonstrate that the new European Zinc-Magnesium-Aluminium family offers a significant potential for performance-increase at OEM's press-shops in addition to the well-known, improved corrosion performance.

* Theoretical targets not including technical tolerances

Chemical composition and phases of the ZM coatings

General principles 'Ternary Phase Diagrams'

Phase diagrams are a graphical representation of the physical states of a substance under different conditions of temperature or pressure. Therefore ternary phase diagrams are constructed by the projection of liquidus surfaces of a three-dimensional diagram (a triangular prism in which temperature is plotted on the vertical axis against the compositions of the components on the base of the prism) onto the compositional ternary diagram. The edges of such diagrams represent in each case one of the originally 3 binary phase diagrams of the components. Within this graph, temperatures are often shown as 'contours'. The intersection of two liquidus surfaces is also projected onto the same compositional ternary and is known as a 'boundary curve'.

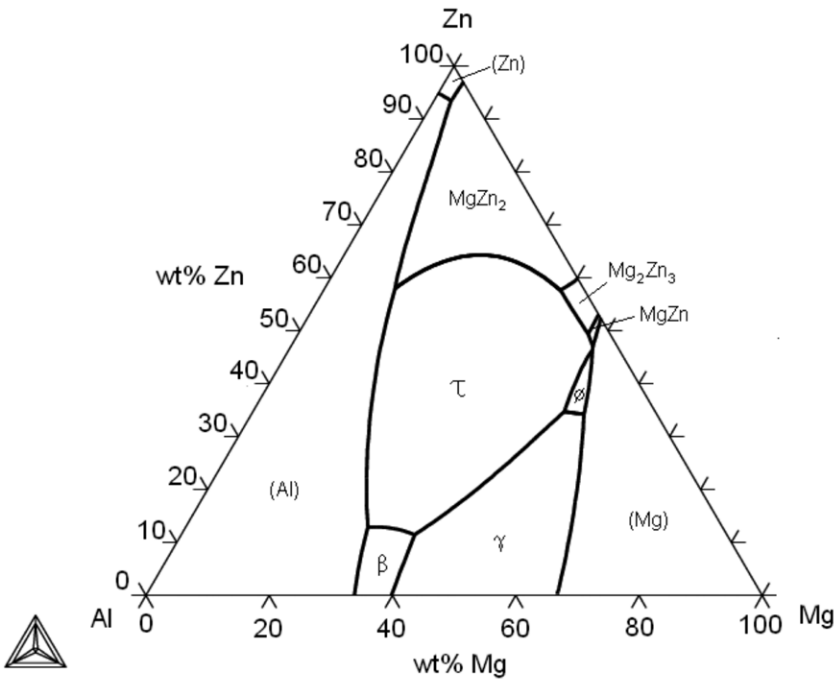


Fig.1: Liquidus surface of the Al-Mg-Zn system

Zn-Mg-Al-Phase Diagram

The Zn-Mg-Al system has a relatively complex equilibrium diagram, see Fig. 1. With regard to the newly developed European ZM alloying systems, only the zinc-rich corner on top of this diagram is of further interest for discussion, see Fig. 2.

In general, by cooling such a liquid film (given by Zn, Mg, Al-content) the prevalent solidification-path will start at the liquidus surface by nucleating a first type of solid phase within the liquid film. With continued cooling the solidification-path will then reach a boundary curve of the ternary system. This initiates nucleation of an additional solid phase within the coating-film and typically ends at the ternary eutectic point by formation of a third (and final) solid phase.

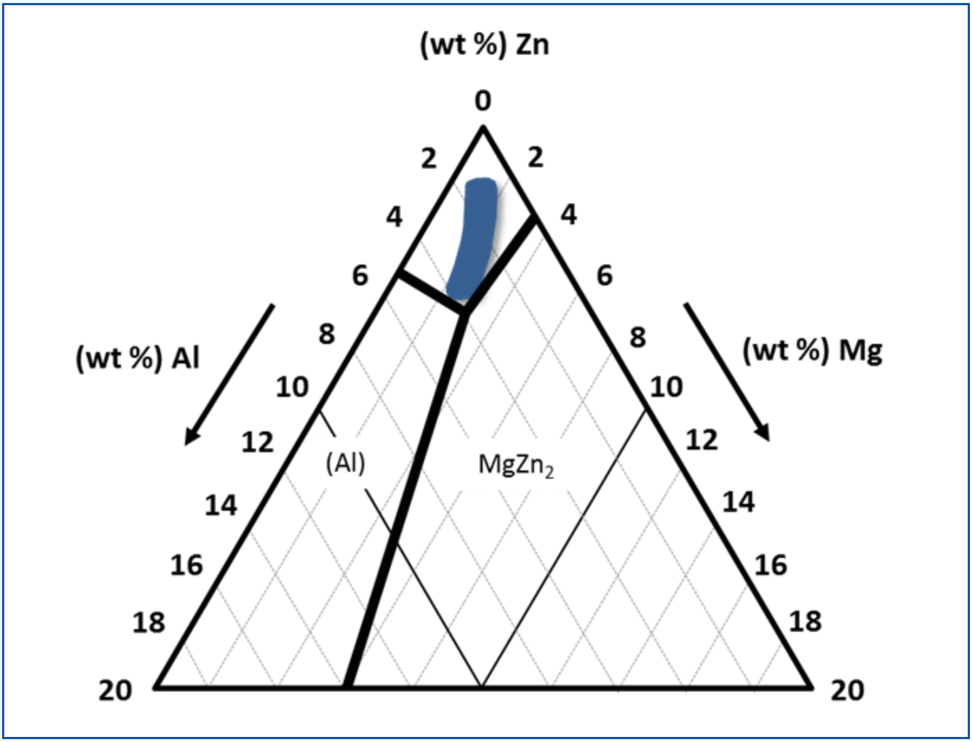


Fig. 2: Zn-rich corner of the liquidus surface of the Al-Mg-Zn System

Since the chemical compositions of the considered European ZM-alloying systems are quite close to each other, solidification processes will take place in a very similar way. Their phase-composition is consisting of the same types of phases. Regardless of the exact path of solidification, solidification will definitely be finished at the ternary eutectic point at approximately 336°C and the following phases will be observed in all of these ZM coatings:

- zinc dendrites (Zn)
- binary eutectic structure ($MgZn_2$, Zn)
- ternary eutectic structure ($MgZn_2$, Zn, Al-rich Zn-phase)

Due to the similar coating compositions it is not surprising that product properties are also settled within a very narrow range, which is also confirmed within the following pages.

In contrast to that, earlier alloying concepts with significantly higher alloying content of Al and Mg behave quite differently in terms of solidification process, coating structure and product properties.

Product properties of ZM coatings

The task of the author group was to achieve comparability in terms of all properties for the various ZM coatings with their differing chemical compositions. Therefore hot-dip galvanised coatings (Z) with the same coating weights were chosen as the base reference. Such Z coatings were also preferred as most of the OEMs have had the most extensive experience with them.

The testing methods are listed below. If established, standard tests were carried out. In those cases, where standard test are not common and various test methods were used, the results were normalized in order to be comparable. The tests used by most members of the group are marked in bold.

The following page will show the product properties of ZM in accordance with SEW 022 (as an addition to DIN EN 10346) in terms of a table as an overview. All testing methods and the results are based on Z100 as a reference coating.

General evaluation of product properties of ZM in comparison to Z

	Z	ZM
Forming		
Adhesion of coating to the sheet	◎	◎
Abrasive tool wear	◎	◎
Tool pollution / Galling	◎	⇑⇑
Tool pollution / Powdering	◎	◎
Friction coefficient and stick slip	◎	⇑
Deep drawing	◎	⇑
Joining		
Spot welding	◎	◎
Laser welding	◎	◎
Adhesive bonding - crash adhesives		
failure mode / fracture pattern	◎	⇓ *
lap shear strength	◎	◎
Adhesive bonding - structural adhesives		
failure mode / fracture pattern	◎	◎
lap shear strength	◎	◎
Adhesive bonding – anti-fluttering products		
failure mode / fracture pattern	◎	◎
lap shear strength	◎	◎
Paintability		
Phosphatibility	◎	◎
Paintability (adhesion dry)	◎	◎
Paintability (adhesion wet)	◎	◎
Stone chipping	◎	◎
Corrosion behaviour		**
Cosmetic corrosion - edge	◎	⇑⇑
Cosmetic corrosion - scribe to metallic coating	◎	⇑⇑
Cosmetic corrosion - scribe to steel	◎	⇑⇑
Flange corrosion	◎	⇑
Stone chipping (with corrosion)	◎	◎
Temporary corrosion protection during transport and storage	◎	◎

* Cohesive failure mode is dependent on specific adhesive systems
** Since corrosion behavior of components is based on the performance of the whole system (metallic coating, phosphating, painting), the specific systems of the customers should be checked

⇑⇑ especially recommended ⇑ recommended ◎ standard

⇓ less appropriate ⇓⇓ not recommended

Note: The information given in this table characterises the current level of experiences.

Forming

Adhesion of coating to the sheet

standard

Adhesion of the metallic coatings of hot-dip galvanised steel sheets is a pre-condition for sufficient corrosion protection, and should not be affected by further processing (i.e. forming). Therefore, adhesion of metallic coatings could be tested by use of a dynamic impact test, in which a steel ball hits a flat sample and forms a local impression. Such dome-shaped impressions subsequently will be ranked by use of adhesion standard series into four levels, from excellent to poor.
Alternatively, bending tests could be performed.

Conforming to ASTM E290, a distinction is made between four different modes of implementation.

- guided bend
- free bend
- bend and flatten
- semi-guided bend

On the convex side of the sample discontinuities, loss of the metallic coating will be evaluated.

Testing methods:

- **SEP 1931 (Ball impact test)**
- **0T bend + taping exterior (180°)**
- Bending through adhesive (90°)

Results:

- **ZM coatings perform equal to Z coatings**

Abrasive tool wear

standard

The term “tool wear” refers to the smoothing of the abrasive tool roughness, which is the result of the processing of metallic coated sheets. Due to the slightly increased hardness of ZM coatings, in contrast to conventional Z coatings, such behaviour has been given special attention.

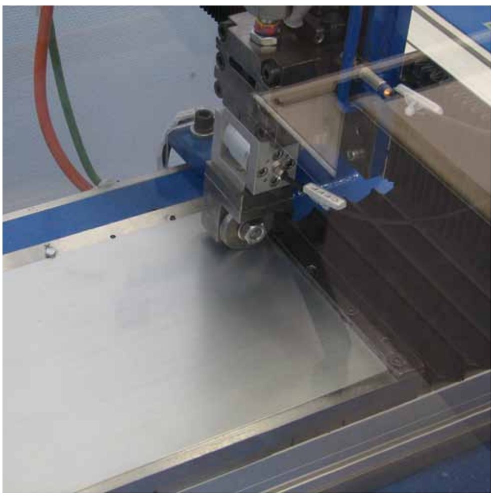
The wear of the tool is detected by measurement of the grooves or roughness of the tool surface.

Testing methods:

- **VDEh SEP 1160/T8** - Evaluation of Weldable Corrosion Protection Primers for the Automotive Industry Part 8: **Tool Wear Behaviour**
- High frequency press (10.000 cups)
- Slider on sheet test

Result:

- **ZM coatings perform equal to Z coatings**



Forming

Tool pollution / Galling

especially recommended

Galling is widely known as material transfer from the work piece (coated steel strip) to the tool surface and usually forms a relatively strong adhesion on it. That is why galling is a type of adhesive wear.

On a laboratory scale, such behaviour is often tested by use of a linear friction tester. (Using well defined axial forces a coated steel strip is drawn through clamps followed by an inspection of the tool surface concerning adhesions).

Testing methods:

- **Linear Friction Test**
- Press trials with OEMs

Results and experiences:

ZM performs much better than Z. There is no galling while processing ZM material, even at higher tool temperatures.

- The results have been verified in customers´ press shops
- This conclusion drawn from lab results is confirmed by field experience in tube mill production of longitudinally welded tubes:
    - ZM-coated material showed good forming properties
    - Less motor power
    - Less emulsion
    - No wear
    - No powdering
    - Lower noise level during production

Forming

Tool pollution / Powdering

standard

Powdering is to be understood as the accumulation of non-adhesive particles on a tool abraded from the coating of the sheet material during forming.

Testing methods:

- **Strip drawing test**
- Cup test
- 60° V-bend test (Honda HES C 502-99 tape interior, width of powder)

Results:

- **ZM coatings are comparable to Z coatings**
- No powdering on ZM coatings

Tribological behaviour

recommended

The coefficient of friction (COF) is a dimensionless scalar value which describes the ratio of the force of friction between two bodies and the force pressing them together. The coefficient of friction depends on the materials used.

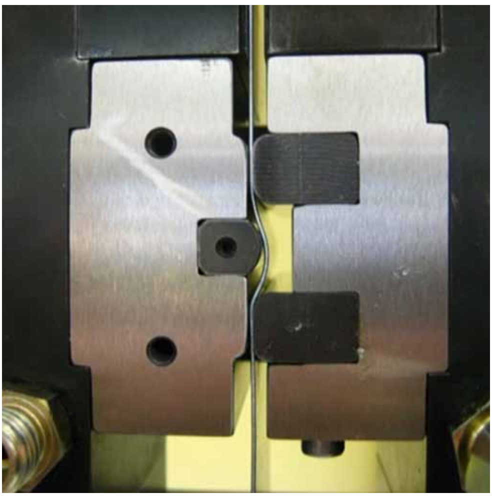
Stick-slip is caused by the surfaces alternating between sticking to each other and sliding over each other, with a corresponding change in the force of friction.

Testing methods:

- **Strip drawing test**
- Rotational friction test

Results:

- **ZM coatings perform better than Z coatings**
- Due to constant low friction coefficient and improved stick-slip behaviour, the blank holder forces can be increased, the working range can be enlarged
- The benefit will be seen during multiple stages in the press shop



Forming

Deep drawing

recommended

Deep drawing is a sheet metal forming process in which a sheet metal blank is radially drawn into a forming die by the mechanical action of a punch. It is thus a shape transformation process with material retention.

Testing methods:

- **Cup test (LDR-Limit drawing ratio)**
- **Deep drawing process window for round pot**

Results:

- **ZM coatings perform slightly better than Z coatings**
- ZM coated material allows an incrementally higher blank holder force due to the delayed stick-slip effect

Joining

Spot welding

standard

Spot welding is a resistance welding method used to join two to three overlapping metal sheets. Usually power sources and welding equipment are sized to the specific thickness and material being welded together.

Influencing factors are:
- Steel grade and sheet thickness
- Coating weight

Tests are implemented using standard procedures. Electrode lifetime and current range were tested.

Testing methods:
- **SEP 1220-1: General specifications**
- **SEP 1220-2: Resistance Spot Welding**
- ISO 18278-2, Resistance welding - Part 2: Alternative procedures for the assessment of sheet steels for spot welding (ISO 18278-2:2004 or EN ISO 18278-2:2004)

Results:
- **ZM coated material in comparison to Z coated material:**
    - barely deviates in position and size of welding current range
    - showed a slightly reduced electrode lifetime (tested at 50 Hz AC)

Laser welding

standard

Laser beam welding is a welding technique used to join multiple pieces of metal through the use of a laser. The beam provides a concentrated heat source, allowing for narrow, deep welds and high welding rates.

Influencing factors are:
- Steel grade and sheet thickness
- Coating weight

Tests are implemented using standard procedures.

Testing methods:
- **SEP 1220-1: Microsections of the weld seam are analysed by means of micrographs: general specifications**
- **SEP 1220-3, the maximum welding speed was determined**
- Visual inspection of the weld seam is performed to detect porosity and spatter

Results:
- **Both products ZM and Z have a similar behaviour in terms of laser weldability**
- No porosities, no spatter in all cases when using an intersheet gap
- Strength, elongation and energy absorption of joints with ZM coatings are comparable to those with Z coatings.

Adhesive bonding

Adhesive bonding is the surface-to-surface joining of similar or dissimilar materials using a non-metallic adhesive substance. Depending on the application of these joints different types of adhesives with different properties (e.g. strength, processing characteristics) are required.

Influencing factors are:
Type of adhesive, metallic coating, coating weight, sheet thickness and steel grade

To compare ZM to Z coatings lap-shear strength and failure modes are determined for different adhesives, different base materials and different ageing conditions.

Testing methods:

- **DIN EN 1465, Adhesives – Determination of tensile lap-shear strength of bonded assemblies**
- SEP 1160-5, Beurteilung schweißgeeigneter Korrosionsschutzprimer für die Automobilindustrie. Teil 5: Prüfung der Klebeignung
- EN ISO 10365, Adhesives - Designation of main failure patterns
- ISO 11343:2003 Adhesives - Determination of dynamic resistance to cleavage of high-strength adhesive bonds under impact conditions – Wedge impact method

Results:

- **In general adhesive bonding properties of ZM are comparable to Z** — standard

---

- Lap shear strength is comparable to Z material — standard

- For adhesives with very high tensile strength (> 25 MPa) the failure mode tends to a higher amount of adhesive failure (less cohesive failure mode) for ZM coatings. This is in particular true with peeling samples — less appropiate

---

- Differences in failure mode diminish after ageing — standard

Phosphatibility

standard

The usual pre-treatment in car manufacturing and painting is a trication phosphating. Therefore the phosphating behaviour of ZM was compared to that of Z, where the evaluation was done using various commercial phosphating systems:

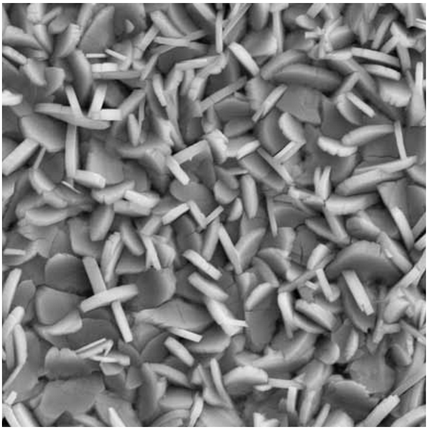
- Surface coverage
- Crystal morphology and size
- Coating weight

Testing methods:

- **Renault OEM Standard D35 1778**
- DIN EN ISO 3892:2002-12: Conversion coatings on metallic materials - Determination of coating mass per unit area - Gravimetric methods (ISO 3892:2000)

Results:

- **Phosphatibility of ZM is comparable to Z**
- Uniform surface coverage
- Phosphate crystal size is equal to crystal size on Z
- Regular layer growth with commercial phosphating chemicals



Adhesion dry and wet

standard

Sufficient paint adhesion is required in order to ensure the mechanical reliability of duplex corrosion protection systems. Various test methods were used to check the adhesion of electro-dip (ED) paints to metallic substrates by testing under dry conditions.
Since all organic coatings have a certain level of water absorption, the paint adhesion is also tested in the wet state. Several standardised test methods were used to determine the adhesion of paints to metallic substrates after wet conditions.

Testing methods:

- NF T30-038; EN ISO 2409: Paints and varnishes - Cross-cut test
- General Motors: GME 60401: Cross-Hatch Test of Organic Coatings
- General Motors-GMW14729: Procedures for High Humidity Test (This procedure describes two options (water fog and wet-bottom) of high humidity testing)
- General Motors-GME 60410: Adhesion of organic coatings after storage in warm water - Delamination Test
- EN ISO 6860: Paints and varnishes - Bend test (conical mandrel). Empirical test for paints, varnishes or related products to assess resistance against cracking or detachment from a metal substrate. It is carried out by bending around a conical mandrel under standard conditions.

Results:

- **Paint adhesion on ZM is achieved on a very high performance level (Cross Hatch GT0), equivalent to Z**
- **Good paint adhesion on ZM also in the wet state, equivalent to Z**
- Well paintable with commercial ED paints

Stone chipping

standard

Stone chipping tests are valuable for checking the mechanical steadiness of paints on metallic coatings.

Influencing factors are:

- Chemical composition used for the pre-treatment process (trication phosphating or other). Investigations were done with trication phosphating
- Composition of the full coating system applied onto the metallic surface and curing conditions

Tests are implemented with some standard OEM painting systems and procedures. Damage of the sample surface is matched automatically or visually with reference pictures.

Testing methods:

- **DIN EN ISO 20567-1:2005 C Determination of stone-chip resistance of coatings. Multi-impact testing**
- Ford BI 157-04 High Performance Stone Chip Resistance Test. Includes water immersion for 72 hours per Ford BI 104-01

Results:

- **Good stone-chip resistance of ZM, equivalent to Z**

Cosmetic corrosion at edges

especially recommended

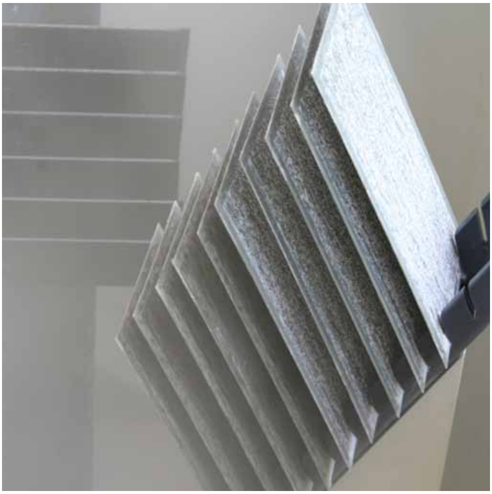
Cosmetic corrosion at edges is a form of corrosion that initiates on a painted cut edge of a vehicle part (e.g. hem flange). After testing, paint delamination is measured in terms of the width of paint creepback from the cut edge.

Testing methods:

- **VDA 621-415**
- VDA 233-102, SEP1850
- Renault ECC1 Test D17 2028/-C

Results:

- **ZM performs significantly better than Z under conventional accelerated corrosion tests**



Corrosion – Cosmetic corrosion

Scribe to metallic coating / to steel


especially recommended

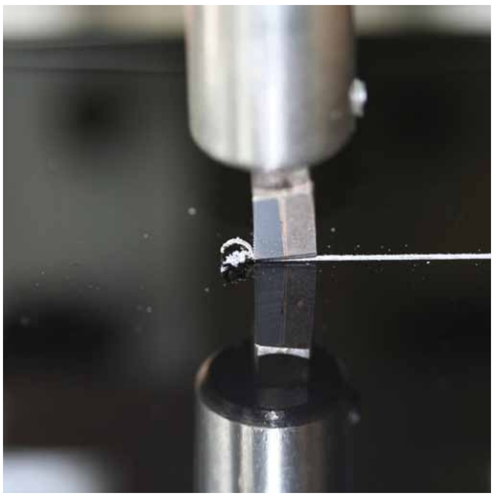
Corrosion that initiates on a visible surface of a vehicle, usually at nicks or scratches in a post-coating, is called cosmetic corrosion. Prior to testing, mechanical damage is introduced to painted test specimens by a cutting tool. The scribe mark penetrates through the paint and pre-treatment layers (phosphate film) into the metallic coating, or in the other case through the metallic coating into the steel base. After testing, paint delamination is compared in terms of the width of paint creepback from the scribe mark.

Testing methods:

- **VDA 621-415**
- **VDA 233-102, SEP1850**
- Renault ECC1 Test D17 2028/-C

Results:

- **ZM coatings perform better than Z coatings under conventional accelerated corrosion tests**



Corrosion

Flange corrosion

recommended

This is the steel perforation corrosion that can take place in a crevice area where salt and water collect. This is tested by a glass panel forming a crevice with a non-ED painted area on a metallic coated steel strip subjected to a cyclic corrosion test. Evaluation criterion are the time taken to the first red rust formation underneath the glass, weight gain during the test and the final steel perforation depth after a certain exposure time.

Testing methods

- **Flange design according to SEP 1160-1**
- **VDA 621-415**
- **VDA 233-102, SEP1850**

Results:

- **ZM performs better than Z under conventional accelerated corrosion tests**

Stone chipping (with corrosion)

standard

These stone chipping tests are valuable for the steadiness of metallic coatings in correlation with the painting in combination with corrosion load.

Influencing factors are:

- Mechanical properties (elasticity) of the painting system
- Type and quality of the pre-treatment
- Stability of the interface metallic coating / paint under corrosion attack

Tests are implemented with standard painting systems (OEMs) and with specified procedure. The damage of samples surface is matched automatically or visually with reference pictures

Test methods:

- **DIN EN ISO 20567-1:2005**
- **Ford BI 157-04 High Performance Stone Chip Resistance Test. Includes water immersion for 72 hours per Ford BI 104-01**
- **VDA 621-415**
- **VDA 233-102, SEP1850**

Results:

- **In general good paint adhesion on ZM, comparable to Z**

Corrosion

Temporary corrosion protection during transport and storage

standard

Temporary corrosion protection helps to avoid changes of product properties before processing at the customer. Temporary corrosion protection is achieved by chemical treatment or oiling at the steel mill. Shipping unprotected material is not recommended.

Testing methods:

- **Humidity Test EN ISO 6270-2**
- **Visual inspection**

Results:

- **ZM performs similar to Z in oiled condition.**
- In unoiled condition, the corrosion kinetics of white rust formation are significantly reduced compared to Z

Summary

All properties of the European ZM coatings and Z as a reference, such as corrosion resistance, forming behaviour, joining and painting ability, were discussed, compared in detail and compiled in this publication.

Based on the automotive standardised tests that have been carried out, similar results were obtained for ZM coatings. This fact is confirmed by the theoretical analysis of the Zn-Mg-Al phase diagram showing that all coatings contain the same metallic phases.

Main conclusions of the tests performed - independent of the European alloying systems* - are:
- Significantly improved forming behaviour
- Improved corrosion performance
- Comparable properties in terms of paintability and joining
- Generally comparable adhesive bonding properties. Fracture patterns dependent on specific customer adhesives

The ZM alloying systems of the European manufacturers are well interchangeable for automotive applications.

* Theoretical targets: Mg [1.0 – 3.0] wt %, Al [1.0 - 3.7] wt %, not including technical tolerances

Literature | Further Reading

- W. Fischer et al: Zinc-Magnesium-Aluminium for Automotive Industry, Galvatech 2013
- W. Warnecke et al: Performance of modern zinc-magnesium hot dip metal coatings, stahl und eisen 129, 2009
- Merkblatt 109, Stahlsorten für oberflächenveredeltes Feinblech; Stahl-Informations-Zentrum, Düsseldorf, 2009
- Charakteristische Merkmale 095, Schmelztauchveredeltes Band und Blech; Stahl-Informations-Zentrum, Düsseldorf, 2010
- SEW 022, Continuously hot-dip coated steel flat products - Zinc-magnesium coatings - Technical delivery conditions; Verlag Stahleisen, Düsseldorf, 2010
- EN 10346 (in progress), Kontinuierlich Schmelztauchveredelte Flacherzeugnisse aus Stahl-Technische Lieferbedingungen
- Zink-Magnesium veredelte Feinbleche; Stahl-Informations-Zentrum, Düsseldorf, 2012

Steel Institute VDEh
at Stahl-Zentrum
Sohnstr. 65 · 40237 Düsseldorf
E-mail: info@vdeh.de · www.stahl-online.de