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The New Family of European ZM Coatings - A Promising Option for the Automotive Industry

Zinc Magnesium Working Group at Steel Institute VDEh

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Summary

From early research work, Zinc-Magnesium-Aluminium coatings (ZM) are well known to be very attractive for corrosion protection. So in the last 10 years, Mg- and Al-contents were adapted for use in the automotive market and combined with the largely optimized and cost-effective hot-dip galvanizing process.

While conducting their researches separately in most cases, European steelmakers converged to form a unique new family of coating systems including the same phases (Zn, Zn_2Mg, Al-rich Zn phase), Magnesium content varying from 1.0 to 3.0 wt % and Aluminium content from 1.0 to 3.7 wt %.

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 form of 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. After intense discussions, the technical characteristics of ZM coatings, which are shown here, were worked out. Moreover, the comparison with all competing systems showed that all European ZM alloys are interchangeable.
Through the example of 'drawing evaluations' in comparison with regular Zinc coating, the process followed by the working group to compare coatings is described. Technical results shared, such as friction or powdering or galling, are

detailed, and demonstrate that new European Zinc-Magnesium-Aluminium coating family offers a significant potential of performance increase at OEM´s press-shops.

A short technical synthesis on tests done dealing with other properties is also given, showing that independent of the composition in the range 1.0 to 3.0 wt % for Magnesium and 1.0 to 3.7 wt % for Aluminium, the performances are at close range.

Key Words
Automotive; coating; properties; ZM; Zinc-Magnesium-Aluminium; forming, joining, corrosion, paintability; properties

Introduction

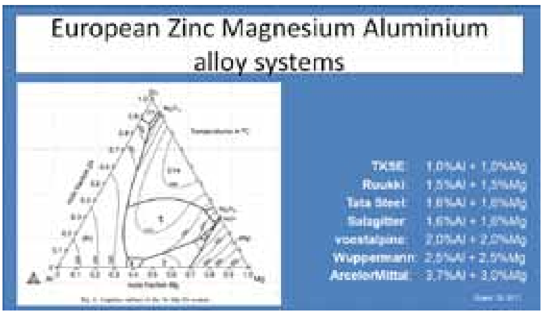

Fig. 1: European ZM alloy systems

Due to worldwide existing patents and patent applications, most manufacturers developed their own ZM products with various compositions of alloying elements (Mg, Al) and registered them with their own product name. So up until 2011, European Hot Dip Galvanizers developed and produced, separately from each other, up to 6 different Zinc-Magnesium-Aluminium coatings (fig.1) for building, as well as for automotive industry.

The comparison of product properties was done in different ways with established coating types (GA, GI, EG, AZ or ZA) as shown in figure 2. These tests were performed individually so in general they were not standardised for - steel grade, strip thickness and/or coating thickness. Of course all of the European ZM producers achieved excellent test results, but due to the individual testing situation these results sometimes differed in absolute values to the results of the competitors.

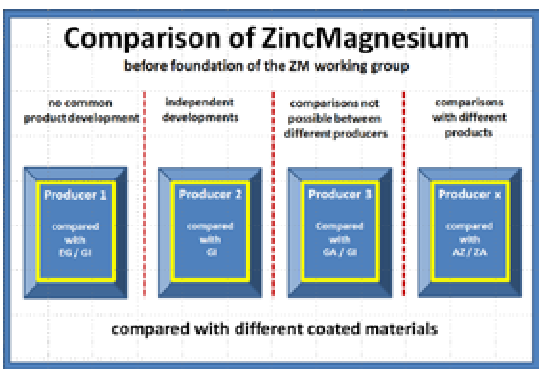

Fig. 2: Comparison of ZM alloys

All of them published their own results on conferences and meetings, such as at the SCT in 2011, and for the audience a question was raised if maybe ONE of those ZM coatings could be better than the rest.

Foundation of VDEh ZM Working Group
To rectify this uncertainty a ZM working group was established at Steel Institute VDEh. Therefore all European manufacturers of hot dip galvanized strip

(ArcelorMittal, Ruukki, Salzgitter, Tata Steel, ThyssenKrupp Steel Europe, voestalpine AG and Wuppermann) sent representatives to identify the potential of all European ZM alloys to the reference standard Zinc, within comparable tests and evaluation methods. In a first step they worked out possible ways to evaluate such new ZM products.

Strategy "A": Each producer has to provide Zinc Magnesium coated samples out of his next campaigns, standardized in steel grade, sheet thickness, coating weight, chemical post treatment, etc. After preparing the samples for several tests, the results will then be collected and cross-checked with the defined standard coating (i.e. Z100).
Strategy „B": Each producer had to look for existing test samples which had already been tested and compared to the coating Z100, and come in with his own testing results, documentation and description of the testing method. Based on these individual results the performance of all ZM coatings could be derived versus standard Z100.
Since strategy "B" probably will be the faster way, this procedure was finally agreed upon within the working group. During the workshops, the status surveys of all product properties, such as corrosion resistance, formability, joining and paintability were shown (fig. 3). These data were then discussed in detail by the experts, compared to Z 100 as well as to all different ZM systems.

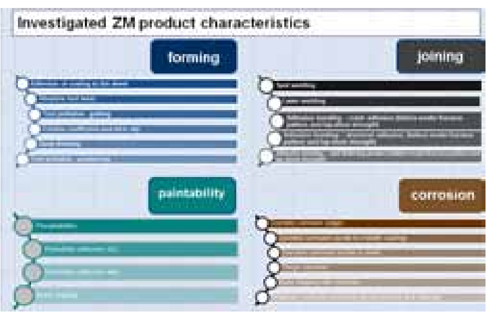

Fig. 3: Investigated ZM product characteristics

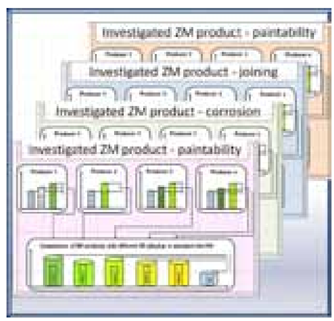

Fig. 4: Schematic of comparison of ZM alloys with standard zinc Z100

Based on those facts, each product characteristic, formally evaluated with common tests standards, had been matched and discussed in detail (fig. 4). At last a comparison of all the ZM systems was carried out and summarised in the brochure "Zinc-Magnesium-Aluminium Coatings For Automotive Industry" (Steel Institute VDEh, 2013) [1].

Forming

When a galvanised steel blank is processed into the desired shape during the forming process, the process stability and component quality is often affected by the abrasion of zinc flakes and galling. The relatively soft zinc coating on steel is normally sensitive to getting scraped off in heavy contact areas with a much harder tool. This often leads to degraded material and high maintenance costs, as well as delays through tool cleaning, increasing the cost price per component. ZM coatings have a higher Vickers hardness compared to Z coatings and therefore have beneficial forming properties.

Due to the higher Vickers hardness of ZM coatings, in contrast to conventional Z coatings, tool wear has been given special attention. The term “tool wear” refers to the abrasive smoothing of the tool roughness, which is the result of the processing of metallic coated sheets and is detected by measurement of the grooves or roughness of the tool surface. The different ZM coatings were tested using the VDEh SEP 1160/T8 test. For that, 2D profiles were measured along the tool width and none of the profiles showed measurable tool wear. The tool wear results for ZM were identical to the Z reference material despite the higher hardness of ZM.

Tool pollution, or galling, is widely known as material transfer from the workpiece (coated steel strip) to the tool surface and usually forms a relatively strong adhesion on the tool. This phenomenon is often tested by the use of a linear friction tester with well-defined axial forces. A coated strip is drawn through clamps, followed by an inspection of the tool surface concerning adhesions. During the test, some zinc flakes were observed on the tool surface when processing Z. These flakes are typical for zinc galling and are well known in press shops. In contrast to that, no flakes could be observed while processing ZM. Therefore the amount of transferred coating material is much less for ZM compared to Z. In addition figure 5 shows some tool specimens after running the linear friction test with Z and ZM coated sheets. There is no galling while processing ZM (fig. 5 b and d) material compared to Z (fig. 5 a and c), even at higher tool temperature (not shown here). These results have been verified in customer`s press trials. Also for ZM coatings, no powdering, the accumulation of non-adhesives particles on a tool, was observed. ZM coatings are very beneficial for components that require high stamping forces such as AHSS or UHSS.

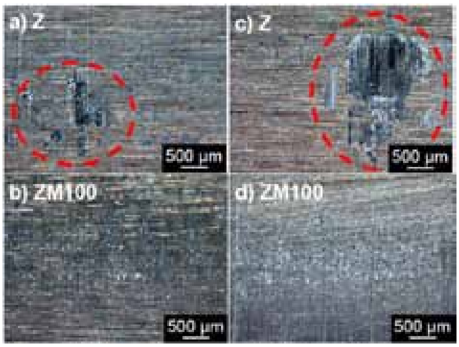

Fig. 5: Tool clamps after linear friction test showing material transfer in case of Z coated sheets (marked areas)

An important parameter is the friction coefficient that allows comparing different materials on their expected performance in the press die. Figure 6 shows the coefficient of friction of Z coated steel, pulled through a clamp, with one rounded and one flat side, several times. The forces in this test are high to simulate the areas in the tool where contact pressures are high. As a result, the friction coefficient of ZM coatings, compared to Z coatings, stays low and quite constant. The increase in the friction

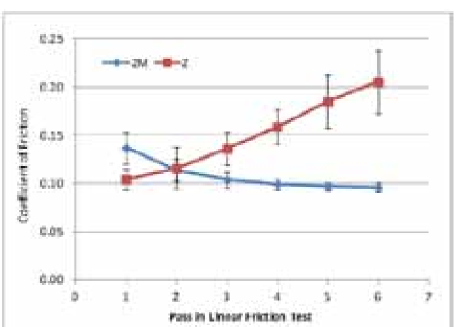

Fig. 6: Development of friction coefficient during strip drawing test

for conventional Z coated steel is most likely due to the scraping of Zinc seen on the tool. For ZM this is not observed due to the increased hardness of the coating. In combination with the verified delayed stick-slip behaviour of ZM, applying a force ramp while running the linear friction test, an improved performance in the press shop is definitely expected for ZM. Due to these advantages, the blank holder force can be increased and therefore the working range can be enlarged. This benefit will be seen during multiple stages in the press shop, especially for deep drawing parts.

In general, and for constant material parameters, the maximum draw depth at fixed blank holder force only depends on tribology of the blank. The lower the friction the larger the maximum draw depth at a fixed blank holder force. This behaviour allows for a comparison of tribology of different coatings under real deep drawing conditions. For predictions of the deep drawing properties of ZM compared to Z, model cups were formed. Based on the behaviour of the two coating systems, it was observed that ZM performed slightly better than Z in terms of tribology, indicating both benefits for ZM and also for deep drawing conditions. This gives opportunity to enlarged working range, especially for complex parts with an increased cracking tendency at the end of the drawing process.

Adhesion of the metallic coatings of hot-dip galvanised steel sheets is a precondition for sufficient corrosion protection, and should not be affected by further processing (i.e. forming). All tested ZM coatings were evaluated using the ASTM1931 (ball impact test) and by using the 0T bend test + taping the exterior side. It was concluded that the coatings adheres equally well to the substrate as well as Z coatings.

Corrosion Protection

Assessment of cosmetic corrosion resistance of ZM coatings has been done using different standard accelerated corrosion tests, which are commonly implemented in the automotive industry [2], [3]: cyclic tests VDA 621-415 and VDA 233-102/SEP 1850 (so-called “New VDA”) and continuous Salt Spray Test (SST) following ISO 9227.The evaluation of ZM coatings has been done in a comparative way together with standard Z coatings.

Cosmetic corrosion results obtained on scratched ED-coated samples after 6 cycles VDA 233-102 show that ZM120 (10 µm/side) coatings present a lower delamination width compared to standard Z140 (10 µm/side) around 0.5 mm wide scratches made either down to steel substrate or down to metallic coating (fig. 7). This result underlines the

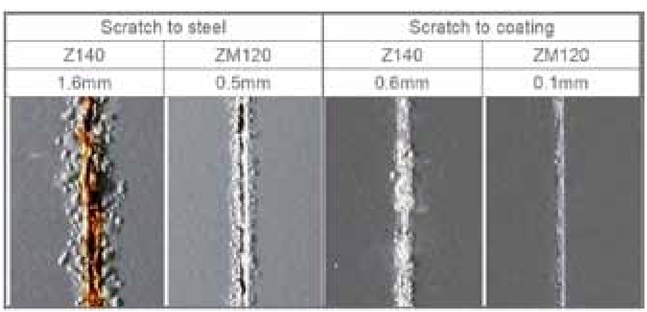

Fig. 7: ED-coated Z140 and ZM120 samples. Delamination around 0.5 mm scratch down to (left) steel substrates and (right) metallic coating after 6 cycles VDA 233-102 test. Figures indicate maximal measured delamination width

superior cosmetic corrosion behaviour of ZM compared to standard Z.

Another type of damage is represented by the stone chipping test according to EN ISO 20567-1, in which the surface of a painted sample is subjected to the projection of chilled iron-grit. This test is used to evaluate the steadiness of the paints on the metallic coating surface and to supply pre-damaged samples for a subsequent corrosion testing in order to allow an evaluation of cosmetic corrosion.

Stone chipping has been used to damage ED-coated ZM120 and Z140 samples and the pre-damaged coatings have been submitted to 6 VDA 233-102 corrosion test cycles. After the test, an optical evaluation of the surface has been performed showing differences in the formation of red rust in damaged areas (fig. 8), highlighting a significantly better performance of the ZM-coated sample in comparison to the Z-coated sample.

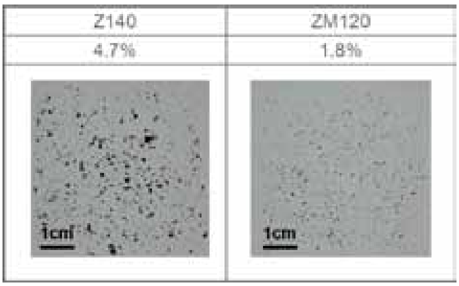

Fig. 8: ED-coated Z140 (left) and ZM120 (right) samples. Optical observation after stone chipping followed by 6 VDA233-102 corrosion test cycles. Figures indicate percentage of damaged area obtained by image analysis

This improved corrosion performance in comparison to a conventional hot-dip Z-coating has been observed also in other tests and with all ZM coatings, which have been evaluated in the framework of this activity.

The better corrosion protection around scratches (paint delamination), which ZM coatings offer in comparison to Z coatings, can be precisely explained based on the example of scratches made down to the steel surface. This phenomenon is first a consequence of the decrease of the oxygen reduction current induced by the coupling between uncoated steel surface at scratch bottom and surrounding ZM coating, leading to a decrease of coating consumption kinetics under the paint in the vicinity of the scratch. In addition, the formation of a protective layer, generated by the reaction of hydroxyl ions with zinc, magnesium and aluminium from the ZM coating and the anions present in the electrolyte can be observed in the scratch bottom. This protective layer has a dense and ordered structure and leads to a further decrease of oxygen reduction current and a decrease of corrosion kinetics. This last phenomenon is the origin of the better performance of ZM coatings compared to Z coatings in the case of scratches down to the metallic coating, or in the case of paint damage resulting from stone chipping.

Joining

Once the different body parts of the car are formed, they have to be joined together to the body-in-white. The most popular joining technology is still resistance spot welding, followed by laser welding and adhesive joining. The latter two become increasingly more important with new developments in car manufacturing. Resistance spot welding has been tested after SEP 1220, parts 1 and 2, and after ISO 18278-2:2004. The welding behaviour of ZM barely deviates from that of Z in position and size of the welding current range; electrode lifetime was slightly reduced when tested at 50Hz AC.

Laser beam welding was evaluated in overlap joints according to SEP 1220 parts 1 and 3. The laser beam provides a concentrated heat source that allows narrow welds and small heat affected zones. Welds with ZM show comparable strength, elongation and energy absorption to those with Z coatings.
Adhesive bonding is carried out with different adhesives according to the function of the seam. Requirements could be e.g. construction, anti-flutter, or sealing. Lap shear testing was carried out on Z and ZM samples according to DIN EN 1465, SEP 1160-5, EN ISO 10365, and ISO 11343:2003. Tests results showed that lap shear strength was comparable between Z and ZM. Some of the tested adhesives with very high tensile strengths, used in crash relevant areas, showed an unexpected fracture mode on ZM samples, where failure mode does not seem to be fully cohesive. This may be a question of a combination of certain adhesives and surfaces. Nevertheless, potential differences in failure mode diminish after aging because of the excellent corrosion protection of ZM coatings. In conclusion, the adhesive bonding properties of ZM coatings are comparable to those on Z.

Paintability

Phosphating is the usual pre-treatment in car manufacturing before painting, as the phosphate layer is the base for a good paint system. Evaluation of phosphating behaviour is carried out regarding surface coverage, crystal morphology and size and coating weight according to Renault OEM standard D35 1778 and DIN EN ISO 3892:2002-12. Regular layer growth was achieved with commercial tri-cation phosphating chemicals, showing uniform surface coverage, where crystal sizes on Z and ZM surfaces were comparable, cf. figure 9. It can be stated that the phosphating behaviour of ZM is comparable to that of Z. Therefore, ZM coatings in combination with automotive paint systems offer improved corrosion protection performance, especially where damages of the paint system occur, e.g. by stone impact, scratches or cutting edges.

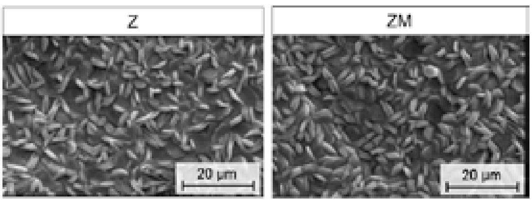

Fig. 9: Phosphate layer morphology on Z vs. ZM

Best Surface Quality

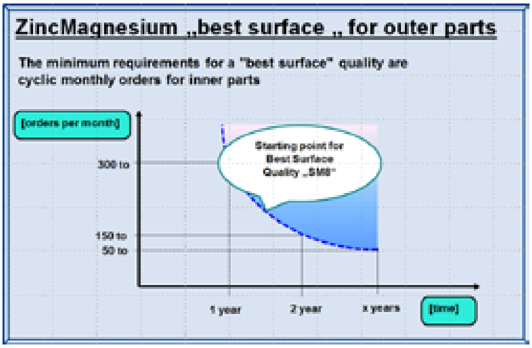

Fig. 10: Schematic draw for the production of best surface quality: order of inner parts versus start of production with best surface quality

In order to offer a reputable series production with best surface quality, support of the automotive industry has to be ensured by continuous orders of inner parts (almost the same steel grade, dimension and coating weight) as shown in figure 10. Only under such conditions the line-setup for best quality could be developed seriously.

Conclusion

As the phase diagram suggests, and as well as the evaluation of the results of the standardised test of automotive industry has shown, the characteristics of all ZM alloy variants are very close to each other.

During the investigations, the ZM manufacturers rated the performance of all ZM products and came to the conclusion that their ZM coatings, including from 1.0 to 3.0 wt % Magnesium and 1.0 to 3.7 wt % Aluminium, exhibit performances in a very narrow range.

In addition to the improved corrosion protection of Zinc-Magnesium-Aluminium-coatings compared to Zinc another very important advantage was clearly observed during the different investigations: the outstanding benefit of ZM in press-shops.
Low abrasion, low tool pollution, and a better friction coefficient open the door to productivity improvement while increasing quality ratio.

Due to this, ZM products provide a promising option for the automotive industry.

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