CORROSION SCIENCE AND TECHNOLOGY, Vol.24, No.6(2025), pp.434~443 pISSN 1598-6462 / eISSN 2288-6524
[Research Paper] DOI: https://doi.org/10.14773/cst.2025.24.6.434

24 Years of Galvanized Autobody Partnership – Highlights and Prospects

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(Received September 19, 2024; Revised September 19, 2024; Accepted November 30, 2024)

Automotive industry requirements continue to drive advancements in the hot-dip galvanizing (HDG) process. While zinc-coated advanced high-strength steels (AHSS) are routinely produced, further improvements are still necessary. To enhance control over AHSS surface uniformity during annealing, computational tools are being developed to predict selective oxidation of alloy elements and surface decarburization. Press-hardened steels (PHS) are increasingly being used to optimize steel utilization in automotive body structures, and advancements in utilizing zinc-coated grades to improve their durability are ongoing. This document describes the effects of processing both galvannealed (GA) and galvanizing (GI) coated precursor grades. A significant cause of HDG process deviations is inaccuracies in pyrometric temperature measurements in the pretreatment furnace. Research on the effects of dewpoints and temperatures on emissivity has been conducted, leading to the development of a predictive model. The contributions of the Galvanized Autobody Partnership (GAP) program—a collaboration between the steel and zinc industries and their suppliers—to these improvements are discussed, along with implications for further technical developments.

Keywords: *Continuous Hot-dip Galvanizing, Surface Decarburization, Press Hardened Steel, Pyrometry, Automotive Steel*

1. Introduction

Prior to 1999, International Zinc Association's (IZA's) predecessor, International Lead Zinc Research Organization (ILZRO) organized cooperative research programs that were open to any zinc-consuming entity that believed they had something to gain from program results. These programs were catalyzed by the decision of automakers of North America and Western Europe around 1987 to broadly apply zinc-coated steel to bodies and structures so that corrosion warranties could be offered to customers. The early programs focused on three main directions: resistance spot weldability of GI coatings, formability of GA coatings and dross control in the galvanizing bath. Many of these results were summarized in the A.R. Marder 2000 review paper sponsored by ILZRO [1]. Initial work concentrated on available IF and HSLA steels, however the continuous move toward higher strength, thinner gauge steels led to new challenges in the galvanizabilty of these grades. It was therefore decided to organize the GAP program, which began in 1999 with the same three Focus Area suites of programs that continue today. These include programs on galvanizability of advanced steels, improvement of galvanizing line operations and performance issues in advanced zinc-coated steels. Highlights of GAP program results since 1999 are presented in this paper, together with future prospects.

2. Galvanizability of Advanced Steels

IF steels were selected for many exterior panel applications in autos of the late 1990's and later because of their excellent formability. However, galvannealing and formability of these grades posed challenges. A GAP-sponsored review at Colorado School of Mines noted the need to closely control Ti and Nb levels. It was recommended that only enough Ti be added to stabilize N and S, and that enough Nb be added to stabilize C. A Ti+Nb stabilized grade with a 60 g/m^2 coating was reported to perform as well as a Ti-stabilized grade with a 30 g/m^2 coating [2].This review formed the basis for

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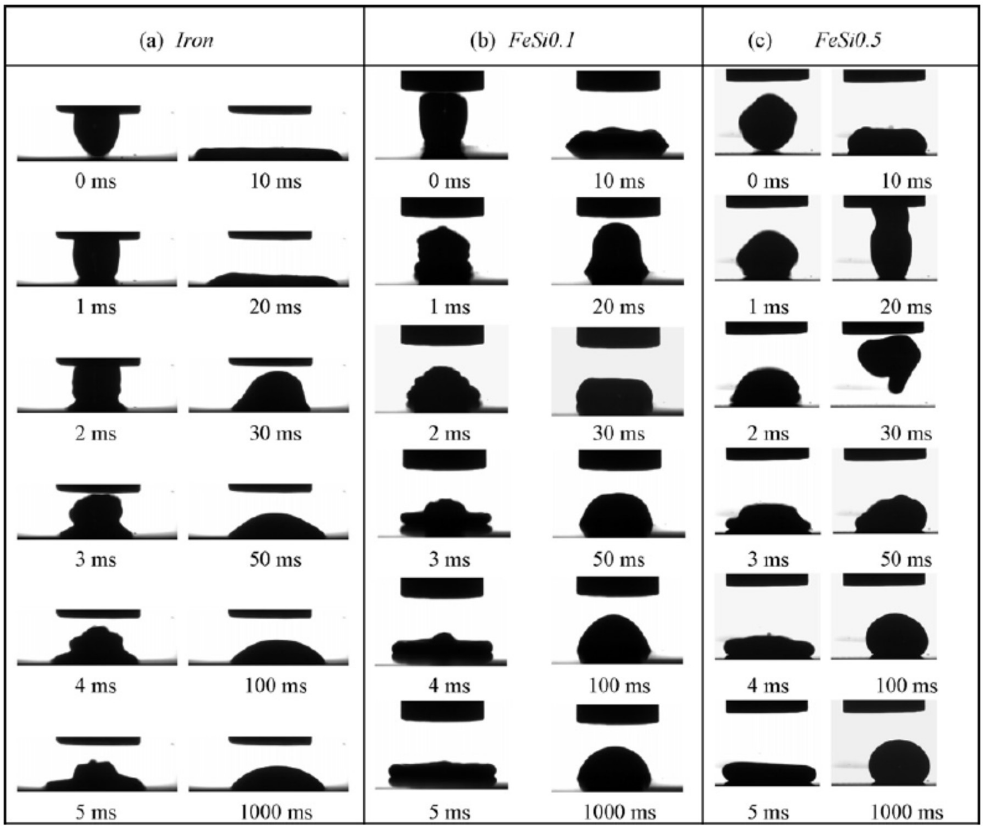


Fig. 1. Droplet spreading behavior of liquid Pb on Fe alloyed with 0, 0.1 and 0.5% Si during dispensed droplet experiments after annealing at 850 ºC for 1h [5]

experimental work on higher strength grades, including steelmaking and galvanized pilot line work at CRM, Liége, Belgium, using a ULC Ti-Nb-P grade with 1.4%Mn. The coating process was optimized to give substrate and microstructures permitting attractive r-values (plastic strain ratio or Lankford coefficient) and tensile properties to be achieved [3].

The fundamental nature of liquid Zn-Al (GI composition) wettability of IF steels was related to oxide particle area coverage, height, and chemical composition [4] This was determined for ULC grades with (0.17Mn, 0.009Si, 0.027Al) and (0.45Mn, 0.074Si, 0.049Al). For the higher alloyed grade, a simulated CGL pretreatment at 800 ºC for 60s at a dewpoint of -40 ºC produced surface coverage by globular oxides that was smaller for the lower alloyed grade, however, the number of surface oxide particles was 5 to 10 times smaller for the higher alloyed than the lower alloyed grades. At the same time, the mean particle area for the higher alloyed grades was 10 times greater. To simplify the analysis of wetting, a non-reactive liquid metal (Pb) was used with binary Fe-Si substrates containing 0, 0.1, and 0.5%Si. Droplet spreading behavior was related to the nature of surface oxide coverage, which was granular in nature for the 0.1% Si composition and filmlike for the higher Si composition after annealing at 850 ºC for 1h [5]. The differences in wetting behavior are shown in Fig. 1.

A very detailed examination of galvannealing behavior of IF steels was made by interrupted heat cycle experiments at CANMET, Ottawa, focusing on intervals during partial Fe2Al(5-x)Znx inhibition layer breakdown [6]. The zinc bath composition in all cases was the “knee point” of 0.135%Al at 460 ºC, saturated with Fe. A low-P Nb-free steel stabilized with 680 ppm Ti exhibited non-uniform breakdown, with deeper attack at emerging Zn-enriched ferrite grain boundaries. Fe-Zn δ crystals nucleated and grew before the inhibition layer was completely enriched by liquid Zn, it is well known that δ can accommodate a relatively wide range of Fe and Zn compositions. After nucleation, the δ crystals reached

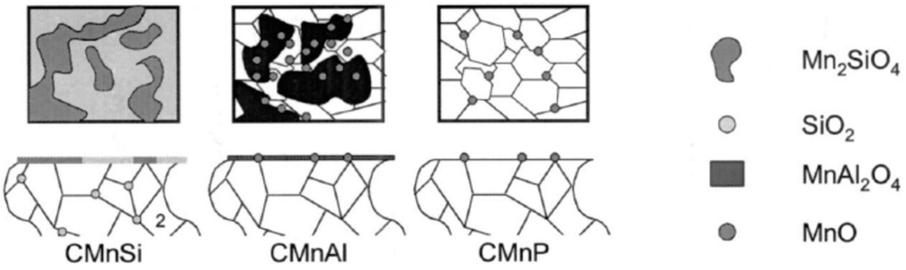


Fig. 2. Overview of the influence of steel composition on the surface state of intercritical annealed TRIP steels, based on combined XPS, SEM and GDOES results [7]

2 μm in height after 2s at 480 ºC. Similar Zn enrichment of ferrite grain boundaries was seen with a (350 ppm Ti, 320 ppm Nb) grade. By contrast, a partially galvannealed (590 ppm P, 360 ppm Ti, 390 ppm Nb) grade did not exhibit Zn enrichment of ferrite grain boundaries; also the breakdown of the inhibition layer in the high-P grade was much slower and the δ crystals were much smaller.

GAP work on TRIP steels began at Univ. of Ghent with a broad fundamental examination of the 3 possible composition families: CMnSi, CMnP and CMnAl [7]. These were subjected to classic CGL treatments, using a dewpoint of -30 ºC for soaking temperatures in the α-γ intercritical range. Surface coverage of SiO_2 and Mn_2SiO_4 prevented galvanizability of the CMnSi grade, while the limited presence of granular $MnAl_2O_4$ and MnO permitted defect-free coatings to be produced on the CMnAl and CMnP grades, respectively, as depicted in Fig. 2. The results of this program were scaled up to a pilot line trial at POSCO's Gwangyang laboratory, where a (0.15% C, 2% Mn, 0.3% Si, 0.8% Al, 500 ppm P) grade was produced and subjected to a CGL treatment including soaking at 827 ºC with a -25 ºC dewpoint, followed by 120 s of austempering at 465 ºC. This gave about 9% retained austenite (γret) for GI processing and 7% (γret) after a 500 ºC GA treatment. Acceptable properties for this 780 MPa grade were obtained with defect-free coatings [8].

It became apparent that control of surface oxidation, especially in higher (>1%) Si compositions was key to successful production of galvanized steel sheet. A fundamental study of this topic was undertaken at Univ. of Delft, resulting in a coupled thermodynamic-kinetic model that can predict internal oxidation behavior of alloy systems in general, with detailed theoretical development and experimental confirmation for FeMnSi, FeMnCr and FeMnSiCr compositions. The best way to process many of the examples considered was reported to be preoxidation to form a surface later of wüstite, followed by reduction of this surface to produce sponge Fe, enabling coatability with Zn [9].

The GAP program research on galvanizability of third generation (martensite-austenite) grades began by considering possible reported routes of producing these grades [10] but settled upon a 6% Mn family of compositions that shows the best potential of meeting property goals while being compatible with existing CGL process parameters. The chosen grades exhibit both TRIP and TWIP deformation mechanisms, are capable of exhibiting defect-free coatings and possess tensile strength-elongation products between 24,000 and 40,000 MPa%. Further details are provided in a paper presented in this same conference [11].

The uptake and property effects of hydrogen are of concern for higher-strength steels. Work at CRM used CGL heat cycles with DP, TRIP and TWIP grades [12]. The DP grades obeyed Sievert's Law, that is, as the hydrogen partial pressure in the furnace gas increased four-fold, the amount of hydrogen uptake in the steel was doubled. There was strong degassing during the overaging part of the CGL cycle. For the TWIP Steel with its high austenite content, not much outgassing occurred below 400 ºC. There was no direct influence of cooling rate on hydrogen pickup, although diffusible hydrogen content was observed to increase as the %H2 in the cooling gas increased. The effect of corrosion on hydrogen uptake was studied using the SAE J2334 test on all 3 coating varieties. All three varieties of steels showed lower amount of diffusible hydrogen in the samples after up to 10 corrosion cycles were performed. There was no pickup of hydrogen in any of the tests. Further work is described in a paper presented at this same conference [13].

Hot press forming using uncoated or Al-Si coated grades is well-developed, however these products do not offer cathodic protection to steel which is highly desirable for many auto body applications [14]. GAP projects determined the mechanisms of microcracking in existing grades utilizing Zn coatings, which is related to liquid Zn-Fe present above the 782 ºC peritectic temperature. High Mn grades that can be processed at lower temperatures, avoiding significant deformation when liquid coating is present, were developed and showed that both suitable cathodic protection and resistance to microcracking could be avoided with Mn levels of 2 and 2.5%, while achieving ultimate tensile strengths greater than 1400 MPa. More detail is provided in a Galvatech 2023 paper on this topic [15].

3. Improvement of Galvanizing Line Operations

At the start of the GAP program, there was only a rudimentary understanding of the principal phenomena related to the galvanizing bath: reactions at the steel surface, nature and control of bath chemistry, and temperature variations in the bath, and the fluid dynamics of the galvanizing operation. Together with other investigators whose contributions have been reviewed [16], the GAP program first determined the nature of Al uptake by the strip in the first few seconds of immersion in work at Université Libre de Bruxelles, Fig. 3, [17], then developed a comprehensive three-dimensional time-stepped model of bath composition, temperature and flow at NRC, Boucherville, Quebec [18]. These computational fluid dynamics simulations identified the rate of formation and the location of dross particles within the bath. The simulations were confirmed by laboratory experiments and industrial trials [19]. Further work modeled the nature of ZnAlMg baths and provided simulations of the formation of top skimmings on the bath surface that arise from the mixing of oxidized bath metal with dross and bath metal, Fig. 4 [20]. In all cases, conditions that improve bath uniformity and reduce the production of dross and top skimmings were determined.

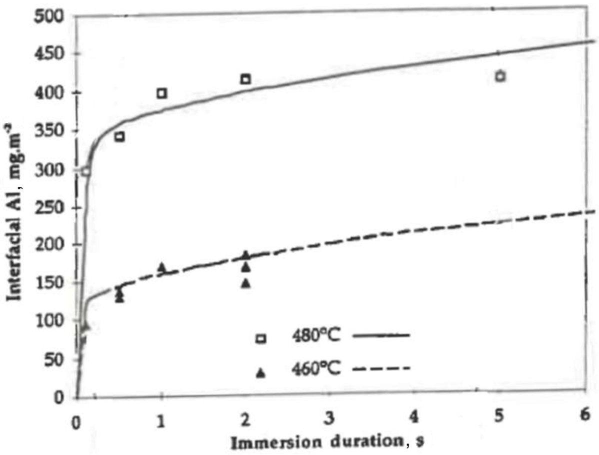


Fig. 3. Effect of bath T on inhibition layer formation, 0.2%Aleff bath [17]

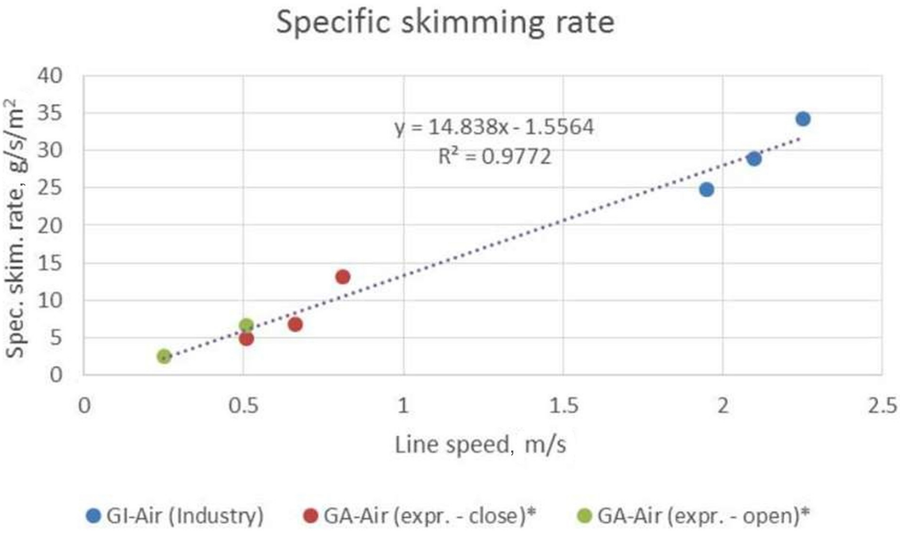


Fig. 4. Specific skimmings production rate for air-wiped GI and GA [20]

Coating thickness (or weight) models available at the start of the GAP program were generally meeting the needs for non-automotive products. A project at McMaster University greatly improved the accuracy of these models for smaller strip-to-knife distances more relevant for automotive products. This determined that the gas pressure profile was not a Gaussian shape, but had a truncated, or flattened, top [21]. Heat transfer in the coating control section was also analyzed, permitting the temperature profile and solidification distance from the wiping knives to be determined [22]. One of the main causes of coating weight variation is the turbulent nature of wiping gas flow. The GAP program developed a multi-slot knife at McMaster Univ. that greatly reduced turbulence variations in the wiping jet. An update will be presented at this Galvatech 2023 conference [22].

The productivity of CGL's is in many cases limited by the useful life of rotating hardware submerged in the bath, i.e. the rolls that guide the strip through the bath. A comprehensive evaluation of existing and new bearing materials by Teck Product Technology Centre included Co- and Fe-based superalloys, cermet coatings and ceramic bearing materials, resulting in rankings of friction behavior and wear rates [23]. This was expanded into two USA Department of Energy sponsored programs at West Virginia University that conducted industrial trials on bearing behavior and the nature of dross buildup [24]. Roll buildup behavior was shown by Univ. of Western Ontario related to roll groove geometry [25] and was comprehensively modeled at Univ. of Leoben to show its relationship to roll surface roughness and line process variables [26]. This work pointed out the need to develop further information on the nature of dross formation and growth, which can be used to further our understanding of this important limitation on productivity and quality [27].

Temperature measurements in CGL furnaces is estimated by pyrometry. Variations in surface roughness and the nature of surface oxide coverage have been linked by GAP researchers at École Polytechnique de Montréal and Univ. of Waterloo to variations in emissivity [28] that result in inaccuracies in measured temperatures used to control furnace power and consequently affect microstructure and mechanical properties of the steel sheet [29]. Improved characterizations of substrate influences and development of models that could improve the interpretation of pyrometry readings will be further described at this conference [30,31].

4. Research on Performance Issues in New Steels

For the automotive industry, the principal issues concerning Zn-coated AHSS relate to formability, weldability and corrosion performance. Early in the development of GA automotive coatings, formability limitations were improved by the application of a light (0.4-0.7 g/m^2) prephosphate coating. Work at Case Western Reserve Univ. indicated that prephosphating

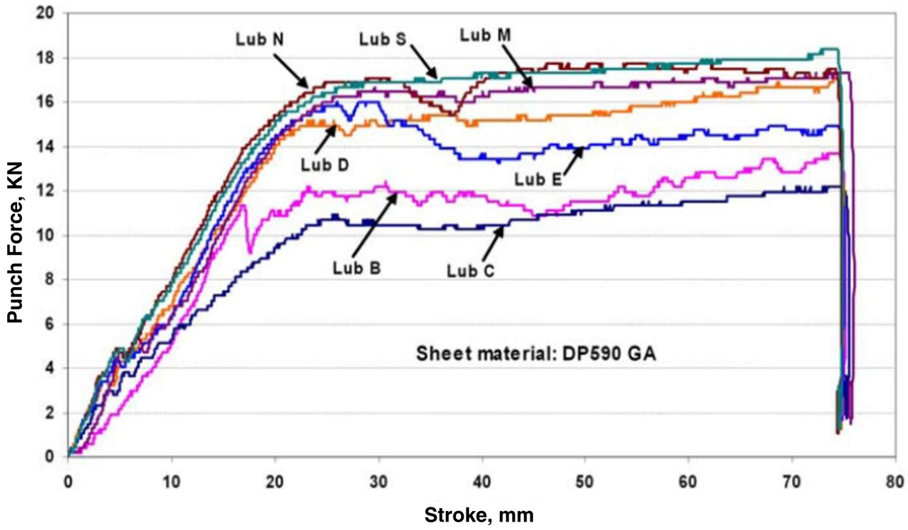
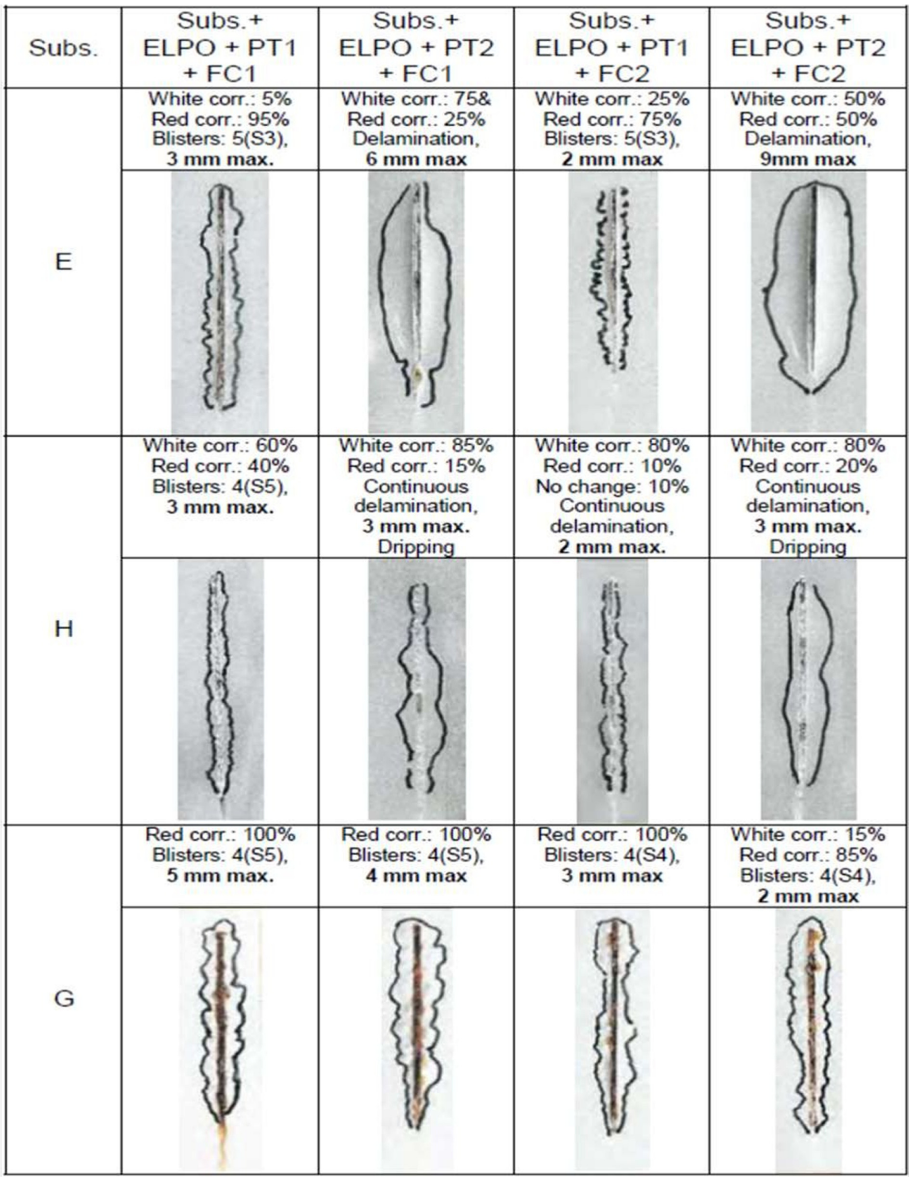


Fig. 5. Load-stroke curves for DP590 GA for various lubricants using an uncoated die [33]

resulted in a reduction of coefficient of friction that was particularly helpful with coatings covered with a layer of zeta phase, although increased powdering in areas of compressive strain could occur [32].

Compared to forming mild steel, the forming of AHSS requires higher contact pressure and temperature at the tool-workpiece interface. This can result in galling, the transfer of coating and substrate from the workpiece to the tool surface. The susceptibility of galling was evaluated for uncoated DP600 and different zinc-coated (EG, GI and GA) AHSS and draw quality steels at Ohio State Univ., recommending lubricant and forming practices to minimize galling, Fig. 5 [33].

Tailor welded blanks (TWB) have become common parts of vehicle bodies and structures. The mechanical properties of Zn-coated DP-HSLA TWB's were assessed for low heat input Nd- YAG and fiber laser welding (FLW) together with higher input FLW at Univ. of Waterloo [34]. The observed soft zone in the heat affected zone (HAZ) on the DP980 side did not reduce tensile properties, because the lowest hardness value in the soft zone was still higher than that of the HSLA base metal (BM). A



Subs.	Subs.+ ELPO + PT1 + FC1	Subs.+ ELPO + PT2 + FC1	Subs.+ ELPO + PT1 + FC2	Subs.+ ELPO + PT2 + FC2
E	White corr.: 5% Red corr.: 95% Blisters: 5(S3), **3 mm max.**	White corr.: 75& Red corr.: 25% Delamination, **6 mm max**	White corr.: 25% Red corr.: 75% Blisters: 5(S3), **2 mm max**	White corr.: 50% Red corr.: 50% Delamination, **9mm max**
H	White corr.: 60% Red corr.: 40% Blisters: 4(S5), **3 mm max.**	White corr.: 85% Red corr.: 15% Continuous delamination, **3 mm max.** Dripping	White corr.: 80% Red corr.: 10% No change: 10% Continuous delamination, **2 mm max.**	White corr.: 80% Red corr.: 20% Continuous delamination, **3 mm max.** Dripping
G	Red corr.: 100% Blisters: 4(S5), **5 mm max.**	Red corr.: 100% Blisters: 4(S5), **4 mm max**	Red corr.: 100% Blisters: 4(S4), **3 mm max**	White corr.: 15% Red corr.: 85% Blisters: 4(S4), **2 mm max**

Fig. 6. Appearance of scribed full finished panels with a 50_1 mm long scribe after 10cycles of VDA621-415 corrosion testing. Zn electrogalvanized (E, top), GI (H, middle), and GA (G, bottom) metallic-coated substrates [41]

joint efficiency of 97–100% was achieved relative to the HSLA grade. Comparing the high to low heat input welds, the fusion zone (FZ) showed more softening in comparison to base metal (BM) (55 HV versus 46 HV) and less bainite (8% versus 15%). The fatigue properties of the high heat input weld were also found to be better than those of the low heat input weld [35].

Under certain metallurgical conditions, zinc-coated advanced high-strength steels have been found to be sensitive to liquid metal embrittlement (LME) arising from joining processes in the presence of liquid zinc when a sufficient stress is imposed. GAP research on LME at Univ. of Waterloo produced a detailed description of the progression of welds where LME was observed and related the location, presence and severity of LME to welding process variables such as weld current cycles and force, electrode misalignment, and metallurgical variables such as grain boundary misorientation and chemistry of the steel and its coating [36,37]. Ways of reducing LME severity included modifications to the electrode shape that reduced faying surface stress and weld cycles that reduced the amount of available liquid Zn [38,39].

GAP work on non-fusion joining (brazing) of Zn-coated AHSS at Univ. of Waterloo showed that GI and GA coatings exhibit different spreading behaviors for the Cu-Si brazing alloys typically used to join galvanized steel sheet. Prior plasma cleaning of both GI and GA samples showed a significant reduction in intermetallic layer thickness as compared with the as-received samples [40].

A comprehensive examination of corrosion performance of EG, GI, and GA-coated panels with full automotive finish systems at INETI Lisbon included traditional primers and new pre-primed treatments, also solvent-based and waterborne base coat-clear coat finish coats. Scribed panels permitted paint adhesion evaluation using a cross-cut method before and after SAE J2334 cyclic testing. Better adhesion was verified on the finish coat with a waterborne base coat. Both finish coats presented good anticorrosion behavior, without significant corrosion attack on undamaged areas. An example is shown in Fig. 6. Regarding the scribe area, the performance was at times observed to be better with the conventional zinc phosphate/immersion primer pretreatment compared to the pre-primed treatment [41].

Much work was done in the GAP program to support the development of ZnAlMg coatings. This included a fundamental study at French Corrosion Institute of the origins of improved corrosion performance of this alloy coating, beginning with confined corrosion exposures typical of automotive hem flanges, that was related to the nature of the corrosion products [42]. Work to further improve performance by quaternary additions found Si, Cr, and Mn to be most promising [43].

Summary

The GAP program has been active for 24 years, working together with Galvanizing steel companies and their connections to develop knowledge on coated steels. Some highlights of the program have been described in this paper. Any companies who find the topics and results of interest is encouraged to join the GAP program so that these kinds of programs are supported in future years.

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