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General vapour-phase galvanizing and duplex coatings.

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Abstract

General vapour-phase galvanizing produces fully alloyed Fe-Zn coatings on steel by exposing complex-shaped articles to hot zinc vapours in vacuum. This way, the processing temperature can be reduced to 350°C. The growth from the gas phase generates microstructures different than other galvanizing technologies. Changing the temperature of growth produces different microstructures in coatings of similar thickness. Mechanical properties are correlated to these microstructures. The chemical properties and the natural roughness of the alloyed surface provide excellent adhesion of the organic topcoat in duplex coatings on vapour-phase galvanized steel. We have performed salt spray and Kesternich tests. The corrosion resistance of bare coatings and duplex coatings are superior to the one of commercial galvanized and galvannealed steels. The specific protocol making general vapour-phase galvanizing possible is presently named as “Epanizing”.

1. Introduction

Up to now, Hot-Dip Galvanizing (HDG) has been the most efficient process to protect iron and steel against corrosion [1-3]. The present paper introduces the scientific information about General Vapour-Phase Galvanizing (GVPG) [4]. The vapour-phase thermochemical process produces a fully alloyed Fe-Zn coating on complex-shaped steel articles by exposing them to zinc vapours in vacuum. The coating protects steel against corrosion. GVPG is a potential substitute to batch HDG.

Batch HDG is a mature process. International norms stabilize the industrial practice [5]. Complex-shaped steel articles can be coated after fabrication. The δ and ζ Fe-Zn intermetallic compounds are the most abundant in the coating. A thin metallic layer of free zinc at the surface, which is 7-11 µm-thick, gives a metallic appearance to the coating. The corrosion resistance
(lifetime) is proportional to the total amount of (free + alloyed) zinc in the coating. HDG coatings, generally between 45 and 85 µm-thick [5], guaranty several decades of protection in natural environment [1, 6].

A 7 to 12 µm-thick layer of pure metallic zinc is produced on steel sheets by continuous HDG [7]. This kind of coating, referred to as galvanized (GI) coating, cannot guarantee long-term protection against corrosion [6]. So, GI sheets are usually finished by an organic paint layer [8, 9]. The skin pass prints a small depth and small pitch roughness that blurs the appearance of zinc grains, makes the surface look dull, and improves the adhesion of the organic layer. Re-melting the coating of dedicated GI steel sheets during 5-20 s between 450°C and 600°C produces a ~10 µm-thick fully alloyed Fe-Zn layer containing mainly the δ, Γ and Γ1 phases [7,10-15]. This re-melting post-process is named « Galvannealing ». Continuous HDG and Galvannealing can only be applied on steel sheets. GI and galvannealed (GA) strips are dedicated for drawing and welding after coating.

Duplex coatings combine a sacrificial Zn-rich coating (for instance: HDG, GI or GA) with an organic topcoat, which improves the protection against corrosion. As a matter of fact, the organic coating delays the oxidation of zinc, and the zinc layer captures the oxidizing molecules that diffuse through the polymer [8, 16, 17]. Since, the lifetime of duplex coatings is highly dependent on the adhesion of the organic layer to the sacrificial layer, sand blasting on batch HDG steel, or conversion treatments on GI sheets, are usually performed before painting to remove zinc oxide and improve the adhesion of the paint. GA layers offer the utmost performance for the fabrication of duplex coatings [16, 18, 19]. In contrast to metallic zinc, Zn-Fe alloys can be painted with a larger range of resins and without a conversion pre-treatment, because the chemical composition and the natural small scale roughness provide excellent adhesion. Moreover, the hardness of Fe-Zn compounds is sufficient to make a conversion layer unnecessary.

Physical Vapour Deposition (PVD) technologies have recently entered the industry for continuous galvanizing. The development of PVD process offers the opportunity of producing intermetallic alloys, potentially in multi-layered or graded structures [20-22]; surface finish able to substitute chromating and phosphating [23, 24]; as well as alternative coatings [21, 22]. Up to now, Zn-Mg alloys have been preferred for continuous PVD on steel sheets because high vapour pressures for Al, Cr, Ni and Ti are hard to achieve. PVD is able to prevent the formation of several Zn-Mg phases. This is an advantage because a composite electrode enables local galvanic currents that accelerate corrosion in liquids [25-27]. Continuous galvanizing by PVD is limited to deposits on steel strips because the cleaning plasma, and vapour sources, must be close to the substrate. Moreover, coating complex-shaped articles by standard (evaporation – condensation) PVD would be complex because vapour condenses in front of the source, and deposition rates strongly depend on geometry. So, a complex fixture tooling would be required in order to randomize the substrate position during deposition, increase the film thickness uniformity, and vary the angle of incidence of the depositing vapour flux [28]. Few attempts have been reported on coating simple-shaped long-products by a careful balance of vapour fluxes coming from different directions. This renders, hollow parts like tubes, impossible to coat that way.

We have developed a protocol able to produce General Vapour-Phase Galvanizing (GVPG)-on complex-shaped steel parts in a batch process in vacuum [4]. According to this process, the temperature of the vacuum vessel is close to the one of the articles to be coated; so, walls and articles themselves act as secondary evaporation sources surrounding parts. On the other hand, the zinc vapour pressure is kept below the dew point of zinc at the temperature of growth. Then,
multiple adsorption and desorption of zinc to and from the surface of the article, as well as to
and from the wall of the vessel, progressively set-up a gas-solid equilibrium; and the vapour
pressure balances at any place of the surface during the reaction. The delay to reach this
equilibrium partially determines the final distribution of zinc in hollow spaces on complex-
shaped parts. The uptake of zinc and the diffusive reaction does not disturb significantly the
gas-solid equilibrium. The rate of formation of the intermetallic compound by diffusion
kinetically controls thickening of the coating.

The particular deposition conditions described above differ radically from the ones used in
continuous PVD galvanizing. Similar conditions in continuous PVD would condense zinc on
entry and exit slits. Our conditions also depart significantly from reactive-PVD where
deposition precedes surface reaction. We refer to « Epanizing » to point out specifically at the
conditions that make GVPG possible in a batch process on complex-shaped pieces. Articles
coated that way are said to be « epanized ». We propose these names as generic names like
« Galvanizing », « Galvannealing » or « Sherardizing » are.

Pioneers have studied the growth of Fe-Zn compounds on steel in zinc vapour: Bastin et al have
recognized that the $\Gamma_1$ and $\delta$ layers grown at the side of Fe/Zn diffusion couples heated at 380°C
resulted from zinc transfer through the vapour phase [29]. Short and Mackowiak have identified
a linear kinetics of growth of the coating on a low-alloyed Armco steel at 500°C, as far as the
duration of the reaction (t) exceeds 50 hours [30, 31]. They have observed that the zinc vapour
pressure and temperature notably influenced the growth rate. The thick coatings were made of
a stack of $\Gamma$, $\Gamma_1$, $\delta$ and $\varsigma$ layers; with the $\delta$ layer being the thickest one. Bretez et al, as well as
Reumont et al, have qualitatively studied the reactivity of low carbon steels (with various
concentrations of silicon) with zinc vapour at 500°C, showing that the intermetallic compound
changed at the surface with the temperature of growth [32, 33]. Additionally, the study of Yu
and Shewmon on pure iron and ultra-low carbon steel has revealed that the out-diffusion of iron
between 550°C and 600°C produced hillocks of the $\Gamma$ phase on the surface at the top of grain
boundaries [34]. Symmetrically, zinc diffused downwards along grain boundaries. Finally,
Schmitz et al exposed two low carbon steels (0.015 wt.% Si and 0.28 wt.% Si) to zinc vapour
in vacuum at 390°C and observed a parabolic growth [35]. Their coatings were only made out
of the $\delta$ and $\Gamma$ phases.

Industrial processes leading to GVPG failed to be developed until now for multiple reasons. On
one hand, Reumont et al obtained negligible rates of growth at 450°C [33]. Similarly, the
growth rates reported by Mackowiak (max ~3.4 µm/h at 500°C [30, 31]) and Schmitz (60 µm
after 19h at 390°C [35]) are about 200 time lower than the one in HDG. Schmitz et al reported
even lower rates at lower temperature [35]. Yu and Shewmon were unable to produce a coating
above 550°C [34]. On the other hand, Short and Mackowiak, as well as Reumont et al, obtained
different thickness of coatings depending on surface orientation at 500°C; and some places have
even not reacted at all after 6 hours [30, 33].

The present article introduces GVPG exploiting conditions of Epanizing. We focus our
attention on the relationship between conditions of growth and the produced microstructure,
and search elements revealing the mechanisms of reaction. We also relate the microstructure to
the functional performances in corrosion. Samples analysed and presented in section « results »
have been selected in order to study the mechanism of growth, which explains the final
microstructure. Samples used for corrosion tests, and for the fabrication of duplex coatings,
have been prepared using the fabrication protocols described in section « methods ».
2. Methods

The patent WO2010/089110A1 describes the process [4]. The experimental set-up (Fig. 1a) includes an oven (1) that can be heated to 450°C or above (2). Articles (3) enter the oven (5), and can be removed (5), through a sealable port (4). The oven is equipped with vacuum pumps (6). Vacuum valves are used for feeding reactive gases, and to enter air into the vacuum vessel at the end of the process (7). The zinc vapour is produced by thermal evaporation (8).

At the laboratory scale, the oven was a simple airtight cylinder (Fig.1b). Surrounding tungsten filaments provided radiative heating. Thermocouples monitored the temperature of the oven at several places. Samples entered the oven from the top; they were fixed to the entry port. Reactive gas and zinc vapours were fed from the bottom. Zinc vapour was produced by a Knudsen cell (not shown). A vacuum valve opened and closed the oven in operation from the bottom (not shown). All these features were inserted into a vacuum chamber equipped with a diffusion pump. The installations developed to test scaling up and using the process in industrial conditions were very similar, but a heat trap has been installed between the chamber and the vacuum pump in order to cool the gas before the pumps [36]. Up scaling and operation up to 100 Pa (background pressure) did not degrade the operations as far as the zinc vapour could propagate in the chamber.

Samples presently presented have been fabricated on low carbon construction steel containing less than 0.1 wt.% Si and ~0.3 wt.% Mn. The fabrication protocol includes a surface preparation step in the air, including degreasing and etching. Presently, etching has been performed in a solution containing 30% of hydrochloric acid and an inhibitor in order to stop the attack when the rust was totally removed. When it can be used, shot blasting is preferred to pickling because it provides a fully dry surface preparation, which reduces the risk of re-oxidizing of steel during drying and the desorption of steam in the vacuum chamber. On the other hand, an abraded surface reacts very well with the zinc vapour. Finally, visual inspection for cleanliness is easier if the work is grit-blasted instead of pickled. Surface activation has been completed into the vacuum chamber by heating pieces at about 450°C in a mixture 5% H$_2$ in N$_2$ in order to reduce...
the native oxides. The sample temperature during the reaction with the zinc vapour can be chosen in the range between 300°C and 600°C. The vacuum vessel is at a temperature close to the one of the articles. The zinc vapour is fed into the vessel after pumping (background pressure below 100 Pa), when the temperature is uniform into the oven. The GVPG reaction is stopped by cooling and admitting the air into the vessel.

Metallurgical microstructures were observed using a JEOL field emission scanning electron microscope (JSM 6500) equipped with a BRUKER – Quantax microanalysis system based on an energy dispersive spectroscopy facility. X-rays for EDX analyses were excited with 20 keV electrons. The lateral resolution of EDX analyses is ~2 µm. It corresponds to the secondary electrons ranges of interactions and to the X-ray fluorescence range of excitation, which far exceed the size of the electron beam. Atomic compositions were evaluated from the EDX measurements using standard ZAF corrections without composition standards. Predictions of the analysis routine have been checked and validated on known samples.

The corrosion resistance of coated steels (in conditions simulating acidic rains / industrial pollution conditions) has been evaluated using the Kesternich test according to ISO 6988. Samples have been exposed to 100% relative humidity atmosphere at a temperature of 40°C with an addition of SO$_2$ during 8 h; and during the following 16 h to the ambient atmosphere at room temperature without SO$_2$.

Reference samples for the corrosion tests have been shot blasted and hot-dip galvanized for a duration of 2 min 35 s at 445°C in an automated industrial plant (GalvaUnion – Escrennes – France), using a commercial galvanizing alloy containing nickel, aluminium, tin and bismuth. HDG levels the roughness of the substrate. The HDG coating was ~70 ± 10 µm thick (min thickness: 51 µm; max thickness: 87 µm). The Fe-Zn layer was 46 ± 6 µm thick, covered by a 32 ± 4 µm thick metallic cap. Thick galvannealed coatings (GA) have been produced by heating the HDG samples described above, during 2 hours at 450°C in air. The metallic cap was fully transformed in iron-rich phases (δ and Γ), as expected [37]. The thick GA coating was ~50 ± 15 µm thick (min thickness: 30 µm; max thickness: 80 µm).

Corrosion resistance of un-painted metallic surfaces have been performed by salt spray at the French Corrosion Institute (Brest) according to the Renault ECC1 D17 2028 procedure (Cyclic Corrosion Test simulating coastal corrosion and winter car underbody corrosion conditions). In the salt spray test chamber (Excal BS 17 5713 - Climats), an atomized 1.0 wt.% NaCl solution (pH 4.1) was sprayed (5.4 ± 0.4 mL/h on a surface of 80 cm$^2$) once a day on the samples placed at an angle of 45° during 50 min. Samples were dried during 95 minutes (relative humidity: 20%), and re-exposed to neutral water vapour 95 minutes (relative humidity: 55%). 5 cycles (80 minutes at 95 % relative humidity + 160 minutes at 55% relative humidity) completed the corrosion test every day. Temperature was kept constant at 35°C. The full test lasted 42 and 84 days (respectively: 1000 and 2000 h). After removal from the chamber, samples were cleaned with deionized water in order to remove loosely attached NaCl residue.

The samples for the ECC1 test were prepared from the same shot blasted plates used for HDG. Sample A has been epanized during 30 min at 450°C; Sample B, during 90 min at 400°C; and sample C, during 60 min at 450°C. The last sample was partially the result of r-PVD (non-equilibrium deposition followed by diffusive reaction). The microstructures of epanized samples produced in these conditions are similar to those described in section 3. The permascope (according to the procedure: ISO 2808) indicated the following thickness: (sample A) 22.5 ± 1 µm, (sample B) 40 ± 5 µm, (sample C) 50 ± 2 µm. These “magnetic” thicknesses provide a statistical average on large area. On epanized samples, thicknesses measured by the
permascopc are larger by an average of ~7 µm than the one observed by SEM on cross section because magnetic measurements require a contact between the sensor and the sample, which is sensitive to hillocks.

Artificial ageing of duplex coatings was performed in neutral salt spray according to the ASTM B117 procedure. Samples have been fabricated as follows. The HDG samples used as a reference are described above. Plates have been etched in an alkaline solution (RBS25 5%) during 10 min at 50°C before spraying the polyester. The three sacrificial epanized layers have been produced as follows: sample D: 500°C – 30 min (thickness: 30µm); sample E: 475°C – 90 min (thickness: 50µm); and, sample F: 400°C – 90 min (thickness: 70 µm) (Fig. 7). The first sample was grown at equilibrium: it is finished by a δ layer. The later were grown in mixed GVPG + r-PVD conditions and are finished by a ζ layer (<10µm). Epanized samples have been painted without any pre-treatment. The polyester powder (PE40) that has been used for producing duplex coatings, had been especially formulated for coating HDG surfaces by Oxyplast (Belgium). The powder has been backed ~10 min at 180°C. The thicknesses of the dried organic layers were ~60 ± 3.5 µm.

Scribes on samples (0.5 mm wide) were produced using a calibrated scratching tool (Elcometer 1538) in order to observe the passivation capability of the corrosion products from the coating, as well as the cathodic delamination of the organic layer in duplex coatings. Scratches went through the organic coating and through the sacrificial layer to the substrate.

3. Results

3.1 Microstructure and composition of intermetallic coatings

Fig. 2 demonstrates the ability of the process to coat the entirety of a complex-shaped piece at once, leaving the epanized surface looking dull grey. The epanized coating is adherent and uniform: it follows the surface shape of the substrate. Eye exam cannot distinguish any shadowing, surface roughness, nor defects.

Figure 2: Demonstration of the ability of GVPG to coat a complex-shape article at once. a) article before coating; b) article after Epanizing.
Fig. 3a and Fig. 3b present electron micrographs of a sample grown at 450°C (60 minutes). The surface is fully covered by a dense coating. A submicron roughness, looking like capillary droplets, decorates the surface, despite the fact that the processing temperature is lower than the melting temperature of the bulk $\varsigma$ (530°C) and $\delta$ (530-665°C) compounds. One of these droplets is pointed by a white arrow on Fig. 3b, and can be seen all over the surface. Thermodynamics suggests that they could be seeds of the $\varsigma$ phase.

Figure 3: Microscopic observation by SEM and analysis of a coating grown at 450°C during 60 minutes. a) top view of the coating; b) closer view of the coating from the top at grazing incidence (45°); c) cross section and observation by SEM; d) EDX analysis along a scan-line from the steel substrate to the top of the epanized layer.

The cross section reveals that the thickness of the layer varies in a range of 15 µm to 30 µm (105 - 210 g/m²) (Fig. 3c). Since the corrosion resistance is recognized to be proportional to the zinc content of the coating, our epanized layer is expected to provide a lifetime 2 to 3 times longer than the one of a commercial GA steel (coating thickness ≈ 8-10 µm). The coating fits the roughness of the steel substrate; but micron-thick additional undulations evidence the growth of oriented dendrites.
Analyses along a scan-line from the interface with steel to the surface, using electron induced X-ray fluorescence (Energy X-ray dispersive analysis - EDX), indicate that the coating composition is between 7-11 wt.% Fe (Fig. 3d). This corresponds to the $\delta$ phase: the same phase as the most abundant one in commercial GA coatings [12-15]. The amount of iron increases at the interface with steel. The $\Gamma_1$ phase, which typically contains between 17 and 19.5 wt.% Fe, is observable at the interface. The constant composition into the sub-layers and space separation suggests the formation of a stack.

Similar compact layered coatings were prepared at 500°C and 550°C (30 minutes). At 500°C, the thicknesses of the intermetallic compounds were respectively: $\delta = 11 \mu$m; $\Gamma_1 = 9 \mu$m and $\Gamma = 12 \mu$m. At 550°C, the thicknesses of the intermetallic compounds were respectively: $\delta = 22 \mu$m; $\Gamma_1 = 5 \mu$m and $\Gamma = 11 \mu$m. The iron content of the $\Gamma$ phase typically ranges from 21 to 28 wt. % Fe. A detailed analysis of reaction kinetics would be cautious from these data because ~15 min are required to reach the reaction temperature. Then, these last samples probably resulted from a growth mode mixing GVPG and r-PVD. Note that the progressive disappearance of the $\Gamma_1$ phase, and its evolution into the $\Gamma$ phase at ~550°C, is consistent with the phase diagram.

Both grain boundaries and cracks can be distinguished from the top (black arrows on Fig. 3b) and on the cross section (black arrow on Fig. 3c). Cracks are due to the fact that the thermal expansion of the coating is larger than the one of the substrate. Cracking proceeds upon cooling and reveals that the coating is under tensile stress after cooling [38, 39]. Processing at lower temperature or the formation of discontinuous coatings should reduce the residual stress. Fortunately, GVPG can be applied under the melting temperature of zinc (419°C) because samples are not dipped in melted zinc. However, lowering the temperature could freeze the reaction since vapour pressure decreases and diffusion slows down with temperature.

SEM observation indicates that lowering the reaction temperature to 390°C modifies the morphology of the Fe-Zn aggregates but does not preclude the formation of the coating (Fig. 4a, Fig. 4b). It confirms the oriented growth of dendrites. The cross section of the layer grown at 390°C demonstrates that a thickness twice the one of commercial GA coatings can be achieved in 30 minutes (Fig. 4c). The chemical analysis reveals that the stack microstructure is blurred (Fig. 4d).

Epanizing at 350°C results in growth of Fe-Zn aggregates on steel (Fig. 5a, Fig. 5b). The comparison of the microstructure of the coatings grown at 390°C (30 min) (Fig. 4c) and 350°C (60 min) (Fig. 5c) suggests that the surface morphology results from the growth of aggregates merging together. The dendritic growth explains the scrambling of intermetallic phases ($\Gamma_1 + \delta$) (Fig. 4d and Fig. 5d).

Comparison of (Fig. 4a and 4b) and (Fig. 5a and 5b) demonstrates that surface activation crucially controls the density of aggregates at 350°C (after 30 min). The variations of the density of nuclei after Epanizing at 350°C could be compared to the so-called “cratering” phenomenon reported after Galvannealing. Surface irregularity after Galvannealing has been attributed to the fact that the reactivity of steel changes from place to place, and that liquid zinc migrates to “high reactivity” areas [40]. The reactivity upon Galvannealing on continuous galvanizing lines is related to the stability of the inhibition layer. The growth upon Epanizing is subordinated to the formation of seeds for $\delta$ grains. When surface cleaning and reduction are sufficient, the epanized layer can fully cover the steel after 30 minutes at 350°C (Fig. 5c).
When cratering occurs due to shorter exposure to zinc vapours, it does not degrade the visual appearance. Faderl et al. also claimed that cratering did not degrade the adherence of the GA coating [12]. This point has not yet been investigated in detail for Epanizing because cratering does not degrade significantly adhesion and corrosion resistance, especially when grid blasting is used for surface preparation. The growth of intermetallic phases during r-PVD departs from this situation because the phase transformation of the deposited metallic zinc first produces filaments of the $\zeta$ phase, and subsequently a layered microstructure.

The comparison of the EDX analyses of Fig. 5d (from the centre of the base to the tip of an aggregate) and Fig. 4d shows that the concentration of iron in the $\Gamma + \Gamma_1$ layer at the interface changes with temperature and duration of exposure. At 350°C, the transformation of the $\Gamma_1$ phase to the $\Gamma$ phase must be correlated to a change in the ratio of Zn and Fe diffusive flux rates.
during the growth. As a consequence, different microstructures can be produced at different temperatures of growth, which provide the same protection against corrosion.

Figure 5: Microscopic observation by SEM and analysis of a coating grown at 350°C during 30 minutes. a) top view of the coating; b) closer view of the coating from the top at grazing incidence (45°). Microscopic observation by SEM and analysis of a coating grown at 350°C during 60 minutes. c) cross section and observation by SEM; d) EDX analysis along a scan-line from the steel substrate to the top of the epanized layer.

3.2 Corrosion tests

The results of Kesternich tests after 40 cycles (40 days) are presented on Fig. 6. The corroded bare steel is fully covered with red rust (Fig. 6a). Traces of red rust have started to appear at the periphery of the HDG steel (Fig. 6b). Metallic zinc remaining at the centre of the plate continues to provide barrier and cathodic protection. The red rust could correspond to the starting corrosion of the \( \zeta \) phase, which significantly contributes to the composition of the intermetallic
underlying multilayer; and which has the lowest electrochemical potential among those of the Fe-Zn compounds. In similar conditions, the epanized steel protected by a layer of the delta phase has not yet been sensibly corroded (Fig. 6c). Moreover, no red rust has evolved at the scribe, indicating that the $\delta$ phase provides both efficient cathodic protection and chemical passivation.

Figure 6: Corroded samples after 40 Kesternich cycles (40 days): a) bare steel; b) HDG steel; c) epanized steel.

Samples were extracted once a week from the test chamber during ECC1 salt spray tests and examined visually. Sample A and HDG displayed the most contrasted situation. Samples B and C, behaved quite similarly to the thick GA one, and in an intermediate way between sample A and HDG. Traces of dissolution and flows of reaction products with various colourations are visible on all samples indicating that corrosion and run off are not uniform.

Table I provides quantitative data related to the ECC1 salt spray tests. Corrosion of the plane surfaces evaluated from image analyses are reported here after six and twelve weeks (respectively, 1000 and 2000 hours) as the percentage of pixels in the yellow-orange range related to the red rust. Run off is presently measured from the reduction of thickness observed
from cross sections by optical and electron microscopy. We have been obliged to measures on cross sections because selective etching was precluded due to the presence of iron in the coatings.

<table>
<thead>
<tr>
<th>Sample</th>
<th>After six weeks of ECC1 tests</th>
<th>After twelve weeks of ECC1 tests</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>% red</td>
</tr>
<tr>
<td>A</td>
<td>20 ± 4</td>
<td>53 ± 3</td>
</tr>
<tr>
<td>B</td>
<td>28 ± 6</td>
<td>8 ± 3</td>
</tr>
<tr>
<td>C</td>
<td>44 ± 3</td>
<td>4 ± 0.5</td>
</tr>
<tr>
<td>GA</td>
<td>50 ± 15</td>
<td>3.5 ± 1</td>
</tr>
<tr>
<td>HDG</td>
<td>70 ± 10</td>
<td>0</td>
</tr>
</tbody>
</table>

Table I: Corrosion of epanized, galvanized and thick galvannealed coatings after ECC1 salt spray tests. (Initial and remaining thickness are in micrometers).

Only white rust is visible on the HDG sample after 12 weeks of exposure to the salt spray (ECC1). No trace of red rust can be distinguished on HDG sample before the metallic zinc cap is fully corroded (% red = 0). Sample A is yet significantly coloured after 6 weeks, indicating that the corrosion protection capability is yet partially exhausted. This explains that red rust goes on accumulating on sample A during the following 6 weeks.

Traces of run off, moderately coloured in red, have appeared on the thick GA sample after 6 weeks of salt spray. They are attributed to the selective oxidation of the iron in the coating. The continuing accumulation of red rust colours further the GA sample after 12 weeks, but the GA sample after 12 weeks is less corroded than sample A after 6 weeks. The coatings on the epanized samples B and C delayed very efficiently corrosion during the first 6 weeks. The reduced colouration of sample C after 12 weeks is probably a consequence of the zinc concentration, which is larger in the epanized layer than in the GA coating.

Close examination at scratches by optical microscopy revealed the following. The diffusion of the zinc corrosion products was able to fully prevent the corrosion of iron at scratches in the HDG sample after 6 and 12 weeks. On alloyed coatings, the colour of scribes was hardly discernible from the plain surface after 6 weeks. However, the cathodic protection and surface passivation by corrosion products of the GA and epanized coatings B and C at scratches were found less efficient than the one of the HDG coating since localized corrosion have appeared from place to place at the scratches after 12 weeks.

The microscopic observation of cross sections of the HDG coating after 6 and 12 weeks of exposure to salt spray (ECC1) reveals the progressive run off of the metallic cap. Microscopic observation of the cross sections of the alloyed coatings confirms their run off, but also reveals that corrosion proceeds preferentially at grain boundaries and cracks. Non uniform corrosion and pitting of alloyed layers have previously been reported by Queiroz and Costa [15]. We have
observed that the cathodic protection is efficient at corrosion pits in thin alloyed coatings since pits reach the steel substrate without entering it. This observation confirms that the discoloration of alloyed coatings (B, C and GA) after six weeks only resulted from the oxidation of the iron from the coating. Corrosion between six and twelve weeks proceeds slower because it is related to the corrosion of remaining hillocks. The anisotropic corrosion, and capping of the Fe-Zn hillocks by corrosion products, reduce the cathodic protection at scribes during this period. Finally, comparison of data related to sample C after 6 and 12 weeks reveals that run off proceeds continuously without colouring the surface in red as densely as the one of the GA sample. This must be correlated to the moderate formation of iron oxides and to the run off of zinc-rich corrosion products.

Fig. 7 presents the results of neutral salt spray tests on duplex coatings (ASTM B117). No blistering, nor point corrosion, occur away from the scribes. This indicates that the PE topcoat is waterproof and that the sacrificial layers prevent efficiently the corrosion by oxidizing species diffusing through the organic layer. After 550 h of exposure to neutral salt spray, traces of white rust flowing from the scribes become visible on the duplex coating based on the thick GI sample (Fig. 7a). Delamination and blistering start from the scribe. The anti-corrosion properties of the duplex system based on GI strongly depend on the adhesion of the organic coating on zinc.

![Figure 7: Results of salt spray corrosion tests at 40°C (angle: 45°) (ASTM B117). a) HDG painted after alkaline treatment RBS25 + exposure to salt spray: 550 h; b to d) painted epanized steel + exposure to salt spray: 1000 h (b: sample D; c: sample E, d: sample F).](image)

After 1000 h of exposure to the neutral salt spray, spots of red rust appear at the bottom of the scribe on the epanized sample with the sacrificial layer 30 µm-thick (sample D) (Fig. 7b). The lateral take-off of the organic layer from the scribe remains narrower than 1 mm, which demonstrates that delamination is efficiently moderated. The other epanized coatings: 50 µm-
thick (sample E) and 70 µm-thick (sample F), are able to prevent both the appearance of the red rust at the scribe (cathodic protection and passivation), and blistering in the vicinity of the scribe after 1000 h (Fig. 7c and 7d). These results demonstrate that GVPG before painting significantly improves the corrosion resistance of duplex coatings to a remarkable standard.

Visual inspection reveal traces of red rust flowing from the scribe after ~100 h of neutral salt spray on painted plates with no sacrificial layer. Marks of white rust flowing from the scribe on HDG based duplex are visible after some hundreds of hours. Fig 7b to 7d show that Epanizing reduces run off, and that the run off of corrosion products leaves marks which are less visible than from other samples.

Examination of cross sections of the painted samples close to scribes sheds some light on mechanisms of degradation after ageing 1000h in neutral salt spray (Fig. 8). The bare steel has been sand blasted before spraying the polyester powder (Fig. 8a). The HDG reference sample has been etched in the alkaline solution as described above before painting (Fig. 8b). The epanized sample has been prepared at 550°C during 90 min (thickness: 55 µm) and painted as such (Fig. 8c). The organic layers were 60 µm-thick.

![Figure 8: Results of the salt spray test (at 40°C, angle: 45°, during 1000 h). Cross sections of painted samples corroded at scribes. a) bare steel (no sacrificial layer); b) galvanized steel; c) epanized steel. (scales are adapted to situations) Please note that scales of Fig. 8a to Fig.8c are different. We were obliged to that choice because mechanisms of degradation proceed at different scales. Fig. 8a reveals that corrosion and run-off of iron dig a trench in the substrate starting from the scribe. Corrosion proceeds under the organic coating and induces debonding. Fig. 8b. reveals that the weakness of the painted HDG sample relies on the adhesion of the organic coating on the GI. Since blistering does not occur](image-url)
far from the scribe (Fig. 7a), it must be assumed that delamination proceeds from the scribe by cathodic corrosion. Zinc has prevented the dissolution of iron. However, the lifetime of the duplex system strongly depends on the adhesion of the organic coating on zinc. Fig. 8c demonstrates that the corrosion products of the sacrificial epanized layer migrate to the scribe bare surface and passivate the scratched steel. Moreover, the corrosion resistance of Fe-Zn compounds avoids cathodic corrosion and keeps the adhesion of the PE layer.

4. Discussion

The epanized coating, which is the product of the diffusive reaction between the steel surface and hot zinc vapour, is a fully alloyed Fe-Zn coating. It is black or grey.

We have experimentally demonstrated that multiple adsorption and desorption of zinc to and from the surface of the article, to and from the wall of the vessel (which acts as a secondary evaporation source) enable the transportation of zinc all over the surface of the sample. The time required to establish the equilibrium could partially determine the final distribution of zinc on complex-shaped parts during the reaction. Additionally, the coating grows at the same rate all over the sample if the temperature is even. As a result, articles do not need to be moved during the reaction in order to get a uniform deposit: complex-shaped steel articles can be coated at once; concave and hollow parts are coated without making shadow, and with no complex handling device.

Epanizing widens the temperature range of production for the fabrication of anticorrosion coatings. Epanizing is a robust process in the sense that about the same amount of zinc is kept in the coating between 350 °C and 450°C. The moderate dependency of the growth rate versus temperature makes the process easy to control. However, surface activation controls the nucleation of the Fe-Zn aggregates at moderate temperatures (350°C – 400°C), and makes the process very sensitive to surface preparation in this range of temperatures.

Reumont et al have observed that the $\Gamma$ and $\Gamma_1$ phases were the first to form at 550°C, and that $\delta$ grew on top [32, 33]. This sequence of nucleation of phases contrasts with the one observed in HDG, in Zn/Fe diffusion-couple and in r-PVD samples, where the $\varsigma$ phase grows first, and which produce a stack of intermetallic layers. Presently, we confirm the preferential growth of the $\delta$ phase from the reaction with the gas phase. This is consistent with a higher mobility of Fe and Zn atoms through the $\delta$ phase, respectively to the one in $\varsigma$ and $\Gamma$ phases, and with a resulting fastest growth of the $\delta$ phase. As a matter of fact, the zinc feed is not limiting the reaction (zinc is in excess on the surface during the reaction).

The temperature of the part controls the rate of growth which is limited by solid-state diffusion. Now, the ratio of the rate of the zinc and iron diffusive fluxes across the layer during the reaction changes with the reaction temperature. Moreover, above 550°C, the $\Gamma_1$ phase is no longer thermodynamically stable. Then, through Epanizing, can be fabricated coatings with similar thickness but different microstructures, by changing the temperature of growth. This offers an opportunity to tune the mechanical properties of the anticorrosion coating. Additionally, the residual stress in coatings epanized in the low range of fabrication temperature are lower than in HDG or in commercial GA coatings. As a matter of fact, no cracks were visible on the fully covering coatings produced at 350°C; and only few cracks appeared at 390°C. This is due to the lower temperature of fabrication and also because the residual stress is released at the grain boundaries between aggregates after the columnar growth.
Epanizing is advisable to produce sacrificial layers in duplex coatings. Samples painted after Epanizing have demonstrated excellent corrosion resistance in standard corrosion tests. The performance of the epanized duplex can be understood as follows. Firstly, 30 to 60 min of reaction produce coatings 2 to 3 times thicker than commercial GA coatings. Secondly, epanized parts show excellent paint-ability; paint adheres very well on Fe-Zn compounds; and the organic coating hinders the migration of the oxidizing molecules to the coating [8, 11, 16, 17]. The excellent adhesion probably results from the chemical composition and the natural small-scale roughness of the epanized layers. It is worth noting that no special priming treatment (nor sand blasting) is required before painting the epanized steel. Thirdly, on one hand, the Fe-Zn compounds are very efficient in preventing paint delamination upon corrosion at scribes, because the Fe-Zn compounds are zinc-rich, so that zinc-corrosion products diffuse, passivate and heal scratches [16, 17]. On the other hand, the electrochemical potentials of Fe-Zn compounds are higher than the one of zinc, making the coating more noble [18, 19, hindering dissolution of the sacrificial layer and the hydrogen evolution. Finally, the continuity of coatings grown at moderate temperature could also be an advantage for the corrosion resistance since Evandro de Azevedo Alvarenga and Vanessa de Freitas Cunha Lins have reported that thermally induced cracking could reduce the barrier protection against corrosion in duplex coatings based on GA coatings, notwithstanding, cracking does not affect the sacrificial and inhibition protections [17].

Epanizing is expected to be advantageous for processing martensitic high strength steels. As a matter of fact, firstly, the dry surface preparation shunts chemical etching and discards any risk of pitting during pickling. Secondly, above 250°C atomic hydrogen is highly mobile in steel, and the hydrogen which could have migrated into the steel degases in vacuum during GVPG [41]. Thirdly, the possibility of hydrogen embrittlement associated to corrosion is reduced when compared to GI steel because the corrosion potential of Fe-Zn compounds is higher than the one of zinc [41, 42]. Finally, Epanizing enables to process pieces at 350°C, preventing tempering of martensite, and preserving the optimal yield and strength of high-strength steels. (Yet, tempering of martensite in modern high strength steels is very limited after batch HDG at about 450°C [39, 43, 44].)

5. Conclusions

The present paper has introduced general vapour-phase galvanizing performed in specific conditions presently referred to as “Epanizing”.

In summary,

- Epanizing can be used to cover steel articles with a fully alloyed Fe-Zn coating, typically 20-30 µm thick. It can coat complex-shaped steel articles.
- Epanizing produces iron-zinc compounds providing outstanding sacrificial and passivating behaviour in duplex coatings. The excellent adhesion of the organic coating results from the chemical properties and the natural roughness of the sacrificial layer produced by GVPG.
- The process can be used at temperatures below 450°C, and down to 350°C. It is especially well adapted for coating high strength steels containing martensite.

All these features make Epanizing a potential competitor to general HDG.
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7. References


