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Challenges to make general vapor phase galvanizing a viable industrial process

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Résumé – Nous présentons une tentative de développement d'une technologie de galvanisation à façon en phase vapeur qui entrerait potentiellement en concurrence avec la galvanisation à façon au trempé à chaud. Cette technologie produit des dépôts intermétalliques Fe-Zn sur l'acier en présence de vapeurs de zinc par une réaction de diffusion. Ces dépôts forment d'excellentes couches sacrificielles pour les revêtements de type duplex destinés à des pièces aux formes complexes. Le papier se concentre sur la présentation des écueils rencontrés lors du passage à l'échelle industrielle. Nous nous intéressons ici principalement au grenailage utilisé pour activer les surfaces avant d'exposer les pièces aux vapeurs de zinc sous vide. Il s'agit de comprendre comment le grenailage influence la croissance des couches. Nous indiquerons quelques pistes qui à notre avis valent la peine d'être explorées dans le futur. Pour faire court, nous proposons de désigner par le terme générique « Epanisation », les conditions particulières que nous utilisons pour la galvanisation à façon en phase vapeur.

Mots clés : Revêtement métallique / galvanisation / anticorrosion / Activation de surface / Germination / IMMAT'2019.

Abstract – We report on an attempt to develop general vapor phase galvanizing for the fabrication of diffusive Fe-Zn intermetallic anticorrosion coatings on steel when it is exposed to zinc vapor. The technology, which is a potential competitor to general hot-dip galvanizing, is especially efficient for producing sacrificial layers for duplex coatings on complex-shape articles. The paper focusses on the stumbling blocks met while upscaling the technology to the industrial level. In particular, we address the activation of surfaces by shot blasting before exposing to hot zinc vapor in vacuum, and how this process influences the growth of the protective coating. Suggestions are made for future studies. For short, we propose to use: "Epanising", as a generic name for referring to our specific protocol for general vapor phase galvanizing.

Key words : Metal coating / Galvanizing / Anticorrosion / Surface activation / Nucleation / IMMAT'2019

1 Introduction

Anticorrosion zinc-rich coatings are fabricated by hot-dip galvanizing (HDG), electro-deposition, metal-spraying, and cementation (Sherardizing). Continuous galvanizing of steel sheets by Physical Vapor Deposition (PVD) is presently commercially emerging.

A challenge to coat complex-shape articles by General Vapor Phase Galvanizing (GVPG) is to get a layer of uniform thickness because vapor goes in vacuum from the source to the substrate in straight line, and deposition rate is highly dependent on the angle of incidence [1]. Flat and long products can be coated by balancing the flux of deposition or by using complex handling devices moving pieces during deposition [1-2]. Complex-shape articles and hollow parts cannot be coated by standard (evaporation – condensation) PVD.

Pioneers have reported that exposing hot iron to zinc vapor in vacuum produces a coating [3-8]. However, Reumont et al got negligible rates of growth at 450°C, and different thickness of coatings on both sides of samples at 500°C [7]. They also reported unreacted areas after 6 hours at 500°C. Short and Mackowiak have reported foreign materials included in the coating, variable thickness depending on surface orientation, as well as extensive fissuring of the coating produced at 500°C [3]. The growth rates reported by Mackowiak (max ~3.4 $\mu\text{m/h}$ at 500°C [3-4]) and Schmitz (60 μm after 19h at 390°C [8]) was about 200 time lower than the one in general HDG. Schmitz et al reported even lower rates at lower temperature [8]. Yu and Shewmon did not aim at producing coating [6].

Improving this concept, we have proposed a fabrication protocol and specific PVD conditions making GVPG possible [9]. Corrosion tests have demonstrated that vapor-phase galvanized samples, and duplex coatings based on them, offer outstanding resistance against corrosion [10]. The next challenges are to succeed the upscaling and to reach sufficient throughput.

The present paper reports success and stumbling blocks met while upscaling the technology. We address here the effect of shot blasting on the activation of steel surfaces before coating. Shot blasting is an advantageous alternative to pickling because a dry surface preparation avoids chemical effluents, reduces the risk of re-oxidizing during drying, and discards the inconvenient of steaming water vapor into the vacuum vessel. Finally, visual inspection for cleanliness is easier if the work is grit-blasted instead of pickled.

2 Methods

The experimental set up (figure 1) includes an oven (1) that can be heated to 550°C (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).

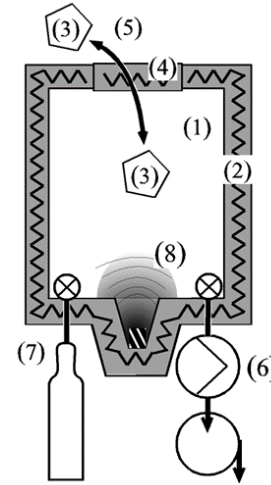


Figure 1. A schematic representation of the experimental set-up for GVPG.

Coatings presented in the present paper have been grown on low carbon hypo-Sandelin steels. Steel surfaces have been shot blasted in an automatic industrial shelter equipped with wind turbines. Shots were: small rounded steel shots (A), large rounded steel shots (B), small angular steel shots (C), large angular cast iron shots (D), corundum shots (E). Blasting conditions were reproducible but poorly characterized. So we refer our results to the surface states after shot blasting as observed by optical and electron microscopy. As expected, examination by optical microscopy and SEM showed that the removal of the oxide scale, surface roughening and mechanical stirring of the steel surface depend on the shots. Chemical analyses by XPS and EDX also revealed surface contamination by the shots (traces of C, S, Si, Al_2O_3). Shot blasting has been completed in-situ by annealing in a mixture of 5% H_2 in N_2 at atmospheric pressure 10 minutes at 450°C. The oxide scale that is not removed by pickling or shot blasting, cannot be reduced by annealing in hydrogen, and prevents the diffusive reaction when it covers more than μm -size areas. On the contrary, the iron native oxides grown after pickling or shot blasting are fully reduced by hydrogen even if steel has been exposed 20 days to the atmosphere after etching or milling. The specificity of our concept consists of keeping simultaneously the temperature of the vacuum vessel close to the one of the articles to be coated; and the zinc vapor pressure below the dew point of zinc at the temperature of growth. Then, the rate of formation of the intermetallic coating is controlled by: the vapor pressure of zinc, the temperature of pieces, and the duration of reaction [4]. The

reaction temperature is in the range between 300°C and 600°C. The zinc vapor is fed into the vessel after pumping below 100 Pa, when the temperature is uniform into the oven. A cold finger can reduce the zinc vapor pressure. The reaction is stopped by cooling and admitting the air into the vessel.

Similar conditions in continuous PVD would condense zinc on entry and exit slits. In r-PVD where zinc vapour condenses first on the surface before alloying, interdiffusion produces first a brittle ζ phase that transforms progressively to the δ phase. The same occurs in general HDG [11-13], and in Zn/Fe interdiffusion-couples [14-15]. On the contrary, our process favours the growth of the δ phase [10]. Thermodynamics imposes the presence of the Γ (and Γ_1) phase at the interface, and traces of the ζ phase at the surface. The growth temperature determines the branching ratio between phases.

In order to distinguish our specific operating protocol from standard PVD and r-PVD, we refer to it as “Epanizing”. Articles treated by GVPG using Epanizing conditions are said to be “epanized”.

3 Results

Upscaling to the industrial level

Technological challenges include: the production of zinc vapor, the stability of tools in the reactive atmosphere, the sealing of the metallic vapors at high temperatures, a uniform distribution of temperature on pieces, and a sufficient control of the heating cycle.

Figure 2 shows a test of up-scaling. The diameter of the chamber was about 0.8 m. The zinc source was separated from the reaction chamber by a hot valve. The reaction chamber and heating elements were into the vacuum chamber. A heat trap avoided overheating of the pump by hot gases [16]. This device operated properly.



a)



b)

Figure 2. The equipment built to develop the process at a larger scale (Umicore). a) The vacuum vessel. b) An overall view of a development set-up.

Figure 3 displays a production unit. Heating elements were outside the vacuum chamber: the reaction was performed in the vacuum chamber. The length of the chamber was about 4 m, and the source was inside the reaction chamber. A standard heat exchanger cooled the gas before the pumps. In operation the zinc source settled a detrimental thermal gradient in the chamber despite radiation shields between the source and the articles.



Figure 3. First industrial set-up (Umicore – Drever International).

Up-scaling was successful with background pressures from 10 to 10^3 Pa, as far as surfaces are not re-oxidized. Reproducibility is highly dependent on the ability of controlling the thermal route (duration / temperature) and preventing thermal gradients within the reaction chamber. The best compromise between surface quality and throughput have been obtained with coating thickness between 25 and 50 μm .

Figure 4 shows articles coated in a set-up similar to the one on figure 3, ~1 m in diameter. Pieces were shot blasted using large and angular steel shots. Surfaces look dull grey. Eye exam cannot distinguish any shadow, surface roughness, nor defects. This demonstrates that complex-shape parts can be coated without a complex handling device.



Figure 4. Complex-shape articles epanized at 400°C during 90 min (coating thickness = 25 μm).

Influence of shot blasting

Shot blasting modifies the roughness of steel (figure 5). Rounded steel shots (A and B) limit the roughening of the steel, but poorly remove the oxide scales. Angular steel shots (C) and angular cast-iron shots (D) efficiently etched the oxide but roughen and stir the surface. Lower density corundum shots (E) are moderately efficient in cleaning, and some alumina grains remain impinged into the surface.

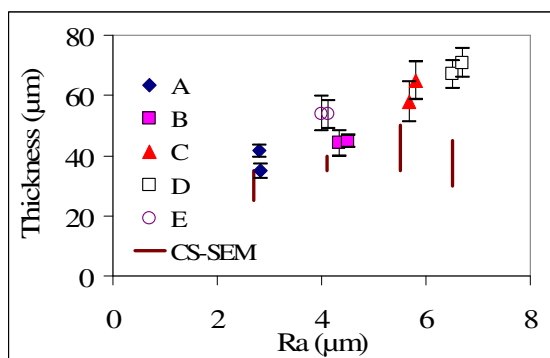


Figure 5. Thickness of coatings epanized at 450°C during 90 min on the shot blasted steel sheets (A to E) versus the roughness after shot blasting (before Epanizing). Measures produced by an (Elcometer) permascope are compared to SEM observations on cross sections on flat matted areas (CS-SEM).

Unreacted bare spots are visible on the surface A, B and E after Epanizing because remaining oxide scales (~ 5 μm thick) prevent the diffusive reaction. Some alumina grains are found into the coating after the diffusive reaction on surface E. Surfaces

treated with shots C and D react properly. Surface activation and cleaning are strongly correlated.

The (Elcometer) permascope measurements of coating thickness after Epanizing suggest that reactivity is related to roughness after shot blasting (figure 5). The observation of cross sections at flat matted areas using the SEM (CS-SEM) refutes this feeling because thickness of coatings apart from strongly roughened places remain constant.

The artefact on the magnetic measurements is due to the fact that the contact method is sensitive to the variation of heights of the highest tips on the surface. At a glance, this explanation seems unsatisfactory on a quantitative basis since the apparent thickness varies over ~25 μm when (Ra) varies over ~5 μm (Figure 5). In fact, (Ra) is the variance of the surface roughness around the average plane; but, point-to-point variations of heights are 2 to 3 times larger than (Ra). Moreover, figure 6 shows that Epanizing amplifies the thickness of the coating on top of surface tips by about 5 μm.

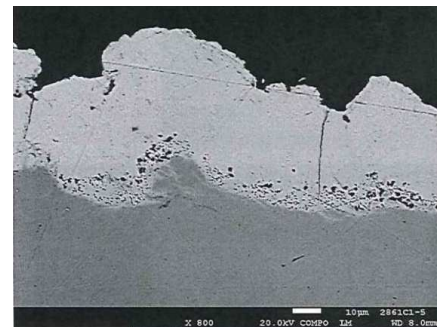


Figure 6. Cross section of a coating epanized at 450°C during 90 min on a steel plate shot blasted with small angular steel shots (C). Observation by SEM at a rough place. (Scale bar = 10 μm).

Figure 7 is a SEM micrograph of a sample epanized at 350°C during 30 minutes. The sample had been prepared by acid pickling and dry reduction of the native oxides in situ.

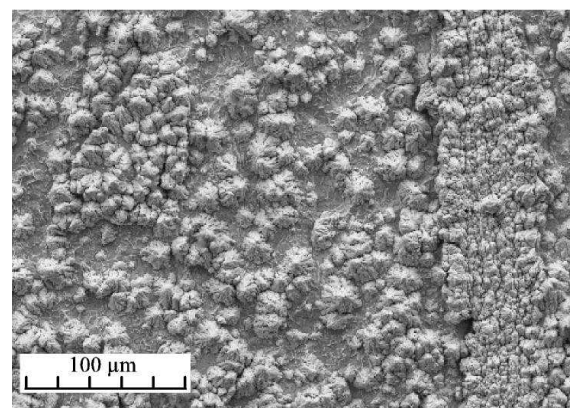


Figure 7. SEM observation of a steel sheet pickled and epanized at 350°C 30 min. Evidence of uneven reactivity associated to uncompleted nucleation step and surface attrition.

The grains in the steel are $\sim 6.6 \mu\text{m}$ in diameter. Then, the colony of aggregates on the left hand side, which is about $80 \mu\text{m}$ in diameter, is not correlated to the grain size of the steel substrate. However, the mean distance between aggregates in this colony corresponds to the one between grains or grain boundaries in the substrate. On the right hand side, a strip of densely nucleated Fe-Zn grains has formed at a scratch on the steel sheet before Epanizing. Surface attrition has stimulated the growth of several nuclei on each single iron grain. On the contrary, in the space between the colony and the strip, the nucleation Fe-Zn aggregates has been delayed at some places. There, the growth is preceded by an "incubation" period [10]. The crystal orientation of α -Fe grains, or the nature of grain boundaries, could explain this situation.

Aggregates are larger in the colony, and between the colony and the strip, than in the densely nucleated strip. This is due to the fact that a dendritic growth selects the shape of the aggregates. The diameters of aggregates are then limited by the available space between neighbor grains. Overlapping triggers the columnar growth.

Figure 7 shows that surface activation expresses the ability to nucleate Fe-Zn aggregates. Sensitivity to surface attrition explains that shot blasting accelerates the nucleation of grains at $T < 390^\circ\text{C}$.

XPS and EDX analyses of pickled steel surfaces have revealed that they were contaminated by calcium, sulfur, carbon and copper traces. Contaminants originated from tap water and from the inhibitor that stops the attack after the removal of the oxide scale. Surface contamination could degrade reactivity while surface defects could provide sites suitable for a stable adsorption of zinc. The hypothesis of a reactivity hindered by contaminants is corroborated by figure 8 that shows a fragment of a submicron thick calcite foil lift out of the surface due to the directional dendritic growth during Epanizing at 350°C .

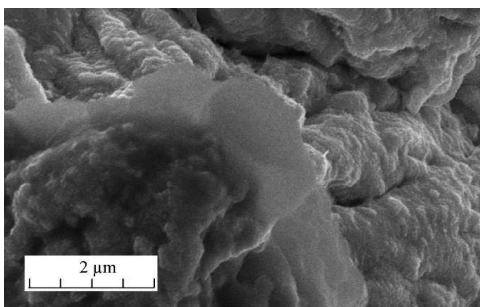


Figure 8. Observation of a submicron calcite foil lift out of the steel surface by the coating after Epanizing at 350°C during 30 min.

The foil has been engrossed by the growing compound, and finally wrapped up by the coating. The same was observed with μm -size fragments of the oxide scale, and Corundum grains impinged in

the steel. Mackowiack reported the same for silica and carbon particles [3].

4 Discussion

Our results demonstrate that surface reactivity must be properly mastered. This explains why previous attempts reported in the literature had failed to evolve to a practicable industrial process [3-8]. To control an even diffusive-reaction requires a reproducible chemical activity.

Below 390°C , nucleation produces an incubation period that delays significantly the start of the diffusive-reaction, and reduce the effective duration of reaction during a batch. Sophisticated cleaning procedures, common in the thin film technology, should be adapted to the metallurgical industry.

Above 400°C , we have not been able to observe the nucleation step because it proceeded fast on every samples. The reaction is easily controlled.

Criticality of surface cleaning and preferential nucleation on grain boundaries suggest that the availability of labile iron atoms trigger nucleation [6]. Dense nucleation on defects generated by surface attrition highlights the importance of surface sites able to stick and pin the adsorbed zinc atoms moving on the surface. The subsequent columnar growth manifests that atomic mobility is not sufficient to densify the coating below 390°C .

Roughness is an additional processing parameter after shot blasting at all reaction temperatures. It is able to change the apparent thickness of the coating by a factor of 2 to 3.

It is known that the roughness of steel affects the growth of the intermetallic phases during hot-dip galvanizing (HDG) because it disturbs the parallelism of the ζ filaments that usually grow perpendicular to the steel during HDG and degrades the passivating capability of the ζ layer in the liquid zinc [11, 12, 17]. The reactivity of steel is similarly increased by mechanical grinding after galvannealing [18].

The directional growth of the reaction product in the 3 technologies is the only similarity that enables to compare the similar influence of surface geometry. Below 390°C , space occupancy by the δ aggregates is determined by the density of nuclei, the shape of aggregates imposed by crystallography, and the local curvature of the steel surface. Above 400°C , the directional growth on surface tips suggests that densification proceeds after a dendritic growth (figure 6).

5 Conclusions

GVPG supplements the panel of technologies for fabricating anticorrosion zinc-rich coatings on steel [9]. Gas-phase reactions are controlled by surface activation, the temperature of the steel substrate, and the duration of the reaction because the growth

is driven by a surface mediated mechanism, which is not directly related to the deposition rate. 25 and 50 μm –thick coating can be obtained in about one hour. This is an acceptable throughput.

Technological challenges for a successful operation include: the production and handling of hot metallic vapor in the vacuum vessel, and the control of the thermal route on every pieces. Temperature uniformity across the batch load could be of particular concern during thermal transients when articles includes parts of various thickness.

Up-scaling has been demonstrated successfully in a set-up up to 4 meter-long with a background pressure between 10 and 1000 Pa. Our experience suggests to prefer an external source of metallic vapor in order to keep flexibility, and to avoid uncontrolled thermal gradient in the oven around the batch load.

Surface activation involves any operation favoring the reaction. To remove the oxide scale is mandatory. Surface cleaning to the atomic scale is also important to stimulate the sticking coefficient of zinc. The production of defects by surface attrition could be a powerful mean to control the nucleation step between 300°C and 390°C. However, the surface roughness produced by shot blasting becomes a concern when it exceeds $\sim 1 \mu\text{m}$ in amplitude.

Epanizing extends galvanizing with a reasonable throughput below 425°C, and potentially down to 350°C. This opportunity could save heating expenses, reduce the thermal stresses induced distortions in complex-shape pieces, and limit the residual stress within the coating after cooling. It is also favorable to keep the mechanical properties of high strength steels. The new process solves important concerns of HDG, and could be a potential competitor to general HDG.

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