# Sn and Ti influence in bending cracks path in hot dip galvanizing coatings

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***ABSTRACT.*** *Hot dip galvanizing processing have remained almost unchanged since over 200 years, but in the last years the attention to environmental topics, leads new approach solution in classical protection techniques, introducing innovative way oriented to optimize different coating properties. Hot-dip galvanizing is a classical processing to generate coatings on iron-based, but many secondary metals added in the bath, for examples Pb important to fluidizing the bath, are dangerous for human health and sometimes is replaced by Sn. Hot dip zinc coated ipersandelin steel specimens were investigated in this work in order to identify the main damaging micromechanisms in intermetallic phases at three different bending angles, considering both chemical composition and intermetallic phases distribution influences. Longitudinal sections of bended specimens were observed by means of a LOM (Light Optical Microscope) and main damage micromechanisms, identified as longitudinal and radial cracks was evaluated.*

## INTRODUCTION

Hot dip galvanizind is one of most important technique to protect iron-base alloy against corrosion in many aggressive environments. The success is due to low production costs and to great properties of protection and adhesion on the protecting substare. Presence of the alloy elements, needed to optimize mainly processes to reduce the scraps, are able to change the traditional intermetallic phases, sometime improuving the mechanical properties of coating, both in the electrochemical processes whether in the hot prosesses [1]. Influence of alloy elements are studied by many authors [2 - 4] either in terms of microstrucutal phases compositions, or in terms of mechanical properties.

Galvanizing are still an important research field to optimize coatings in microstructure changes or some properties such as substrate adherence, corrosion behavior or simply external aspects, through the addition of alloying elements or different pretreatments. Another galvanizing field is in concrete constriction where studies by means of SEM and EDX analysis showed that corrosion products formed on passivated HDG is more stable in test electrolyte than on unpassivated surface.

Furthermore studies also indicate that tests based on potential measurements can be developed to assess the performance of a passivator for zinc coated rebars exposed in concrete pore solution [5].

Zinc-based coating layer formation is obtained by interdiffusion of zinc and iron atoms to generate a layer characterized by different chemical composition leading to a different intermetallic phases according with Zn-Fe diagram showed in Figure 1. From the iron-coating interface to external surface there are different intermetallic phases, which Zn content increases. Therefore the zinc coating is a multilayer system meanly formed by four phases (Figure 1), characterized by different, thickness and mechanical properties. Outer layer is a ductile η phase with maximum Fe content up to 0.03%. The subsequent layer is named as ζ phase, which is isomorphous with a monoclinic unit cell and an atomic structure that contains a Fe atom and a Zn atom surrounded by 12 Zn atoms at the vertices of a slightly distorted icosahedron. The icosahedra link together to form chains and the linked chains pack together in a hexagonal array [5]. δ phase is a brittle one with a Fe content up to 11.5 wt%, with an hexagonal crystal structure. The last phase is a very thin layer named Γ phase and is characterized by a Fe content up to 29 wt% (fcc). Coating formation is governed by physical parameters (bath temperature, immersion time, pre-galvanizing surface temperature, etc.) and chemical parameters (bath and steel chemical compositions, flux chemical composition, etc.).

Processes are very important also on typologies of coatings; eg. in the galvanized steel strip, produced through a continuous hot-dip galvanizing process, the thickness of the adhered zinc film must be controlled by impinging a thin plane nitrogen gas jet [6].

In the last years, there has been an increase in zinc coatings research, focusing both coating procedures and mechanical behaviour characterization, in order to optimize Zn layer thickness and mechanical performances [7]. Three kind of research can be classified to develop the optimizations, the first about material, when it is possible to choice it, the second is about pre-treatment, where it is possible to define chemical composition of flux or different temperature of pre-heat, and finally about chemical composition of the bath.

Presence of silicon in the material is very important to coatings formation and their properties. An excessive contents in steels accumulates on the surface of substrate due to the limited solubility of silicon in the Γ layer. Due to Fe/Zn reaction that determines movement of the α-Fe/Γ interface towards the steel substrate, the α-Fe reach in silicon breaks and the particles enters in to λ layer through the Γ layer due to low solubility of silicon-rich α-Fe in the Γ layer. Then silicon-rich α-Fe dissolving in the λ layer and accelerates the growth of the λ layer to steel substrate, and the coating becomes loose [8].

Studies about pregalvanizing treatment shows firstly that it is possible to replace the conventional industrial chloride flux used in galvanization by a vegetable oil like the linseed oil. Moreover it is also possible to use a mineral oil added with an acid function. Presence of mineral oil well protects the steel but its effects on galvanization is not so well. However addition of hydrochloric acid in the oil leads to improvements coated areas and adherence. Also natural fatty acid used in the flux operation leads to good galvanizations due to its light acidity [9].

Other studies on the bath additions in the bath were carried out in order to evaluate the effects of alloying on the coating formation. For example in the last years the effect of strontium on the adhesive strength and corrosion resistance of hot-dip galvanized coating is studied. Presence of strontium improves both the properties through dendritic grain refinement (86% of grains refinements at 0.002 wt%), adhesion strength (best values at 33%) and corrosion resistance (at 30%) [10].

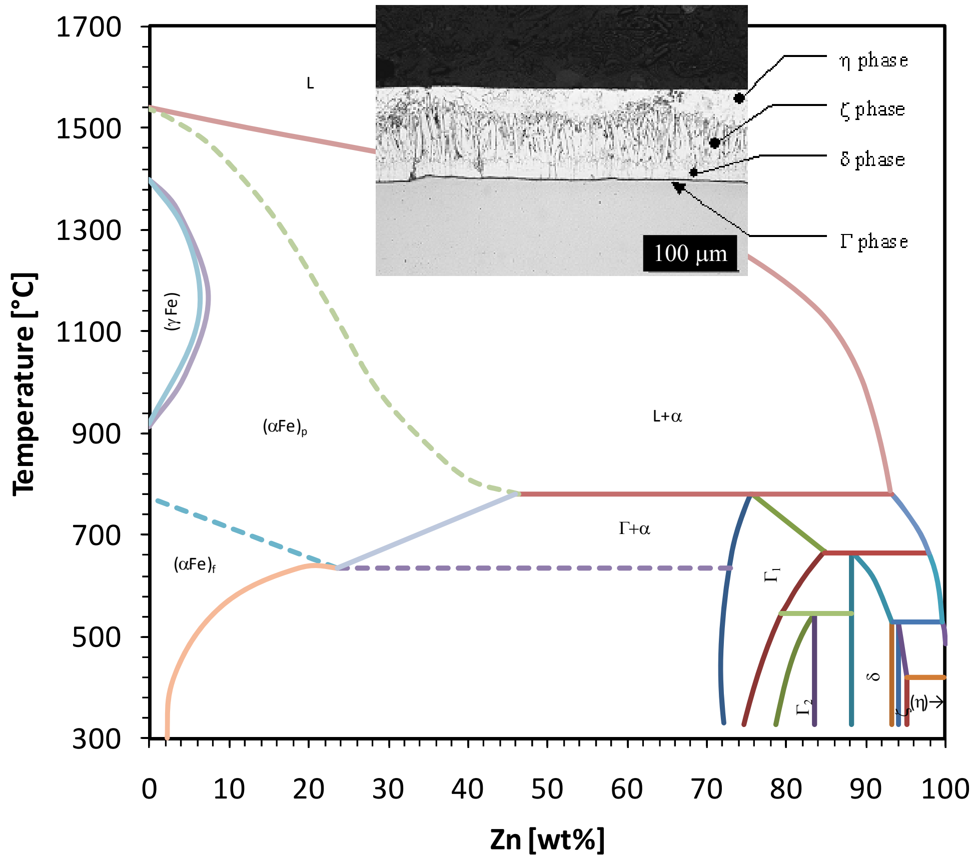



Figure 1: Zinc Coating phases distribution

Another study shows that the influence of the $SiO_2$:$Na_2O$ molar ratio of silicate solution on the properties of silicate coatings on electrochemical tests in comparison to HDG, is an decrease of the corrosion current densities, and an increase of the polarization resistance and the total impedance values, enhancing the corrosion resistance [11].

In order to painting to get a good adhesion, on the galvanized surface an organofunctional silane is deposited on hot-dip galvanized cold rolled steel, where γ-MPS treated samples. Low silane concentration gives a smooth appearance film and higher silane concentrations lead to more cracks in the silane film and ultimately detachment [12].

When coated steel sheets are subjected to corrosive environments, their corrosion behaviour are affected, due not only to changes of the coating texture, but also of the microstructure. Basal plane texture coefficient and would increase at lead content of zinc bath increasing, as well as would increase the texture coefficient of high angle pyramidal, low angle pyramidal and prism planes. Γ layer thickness would be increased with increasing the lead content of the zinc bath. Coatings that have a better corrosion resistance are characterized by greater basal texture coefficient and smaller Γ layer thickness [13].

To prevent the penetration of the aggressive ion $Cl^-$ in the outdoor exposition, a presence of oxid under coating are accepted. Moreover the galvanic performance of the coating improves by the presence of ZnO-rich inner alloy layers as also evidenced when polarization studies were conducted with a different approach [8].

Damage of intermetallic phases, due to mechanical deformation, is an important parameter which influences the corrosion behavior of coatings [14].

## MATERIAL AND EXPERIMENTAL METHODS

Two Zn baths characterized by presence of 3wt% Sn and 0.5wt% Ti are used at 460°C ± 2 °C in order to generate coatings in 60s of dipping time. Specimens to galvanize are o on plates specimens. Specimens to be coated are made from 3mm thick hot rolled plate, in rectangular shape 80x25mm with presence of two hole to held the clamping head. Presence of 0.167wt% of silicon in steel (Tab. 1) provides an ipersandelin behaviour, characterized by high reactivity in zn-based baths.

Table 1. Galvanized steel chemical composition (wt%).

| C | Si | Mn | P | S | Al |
|---|---|---|---|---|---|
| .090 | .167 | .540 | .010 | .004 | .051 |

Prior to galvanizing, steels samples were degreased and rinsed with alcohol. Subsequently specimens were pickled in an aqueous solution 50% HCl at 25°C for 10 minutes, washed in fresh water, fluxed in an aqueous solution containing 280 g/l $ZnCl_2$ and 220 g/l $NH_4Cl$ at laboratory temperature for 2 minutes and then dried for 10 minutes at 50°C.

Static bending tests were performed considering a non-standard device and repeated four times for each investigated coating bath. Tests were performed using an electromechanical 100kN testing machine, considering a crosshead displacement range between 0 and 35 mm, that corresponds to bending angles range between 0° and 38°.

Finally, in order to identify the damaging mechanisms for each investigated coating baths, longitudinal sections of the bended specimens were metallografically obtained and observed by means of an optical microscope (LOM). Damage level was evaluated in terms of “radial cracks density” (cracks number/length) considering 6 images for each specimen (damage level is obtained as the mean value of 24 measurements, with a very high repeability). Crack paths were also evaluated analysing their interactions with Zn-based intermetallic phases. As a consequence, damage evaluation was considered as strongly connected with cracks nucleation: authors are conscious of the limit of this definition that do not take into account the crack growth in the different phases.

Damage and crack path analysis were performed considering different specimens after three bending half-angles, wich leads to respectively 10, 20 and 30° of residual plastic deformation half angle in uncoated specimens.

## RESULTS AND DISCUSSION

Unlike as traditional coatings obtained from Zn-Sn baths, coatings from Ti bath are characterized by violet surface as result of Ti oxidation at high temperature of Zn-Ti “wetted” surface. Presence of Ti in the bath leads to coatings characterized by an inner and an outer zone. Inner zone are characterized by presence of a well developed “δ-like” phase, placed parallel way to substrate. Outer zone are characterized by presence of a double matrix phases (with respectively comapact and lamellar morphologies) and a dispersed phase. Microindentations (Fig. 3) show four microhardness values; smaller values are founded for two phases of matrix and higher for the dispersed phase, wich main values are greater than substrate steel microhardness.

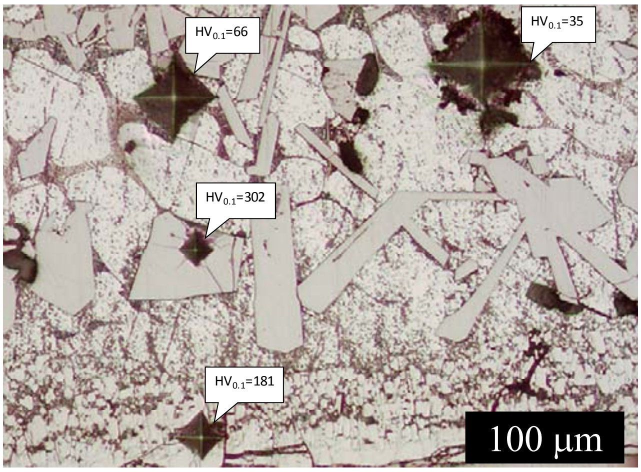
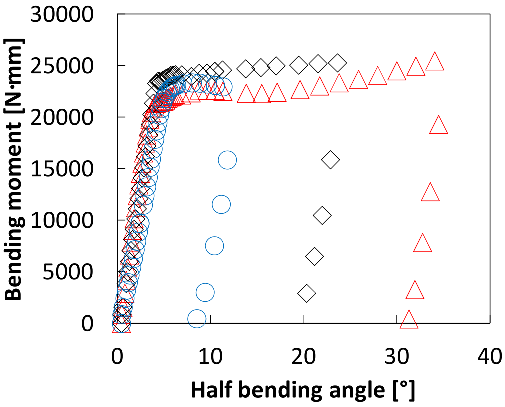


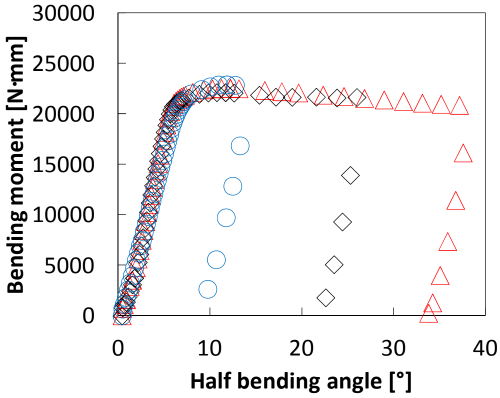

Figure 3: Microhardness of external zone phases.

For these results would be plausible to assume a brittle behaviour for dispersed and “δ-like” phases and a ductile behaviour for each phases of outer zone matrix.

Fig. 4 shows bending behaviour of coated specimens at three deformation angles. Specimens coated in Zn-Sn3% bath show greater strength to bending deformation, and good elastic recovery. Zn-Ti0.5% coated specimens are characterized by a less bending strength and low capability to recover shape for all investigated angles, presumably due to brittle behaviour of coating.




a)

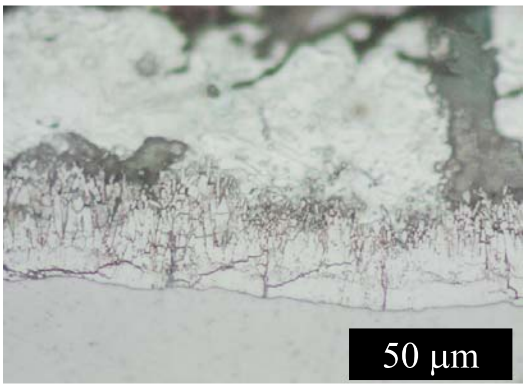



b)

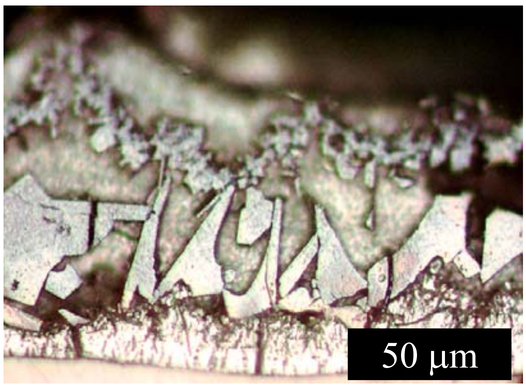
Figure 4: Bending behaviour of coated specimens: a) Zn-Sn3% bath, b) Zn-Ti0.5% bath.

Light optical microscopy analises show presence of intermetallica phases cracks mainly in δ pahase ethier in Zn-Sn and in Zn-Ti coatings as in Fig. 5.

In Zn-Sn coatings (i.e. Fig. 5a)cracks initiate at substrate-δ phase interface and propagate in δ, someones arrested at δ-ζ interface and other ones propagate in ζ phase. Craks in ζ phase, arrested in wich phases or propagate to ζ-η interface. No one cracks initiate in ζ phase and no one cracks initiate or propagate propagate in η phase in all investigated bending angles.




a)




b)

Figure 5: Intermetallic phases cracks path under tensile stress: a) Zn-Sn3% coating bath, b) Zn-Ti0.5% coating bath.

In Zn-Ti coatings, cracks initiate at substrate-δ interface and propagate in δ phase arresting to δ –ductile matrix interface.

In presence of dispersed phase grains at δ interface, cracks propagate in dispersed phases and if grains of dispersed phases are in chain shape from δ to outer surface, it is possible to propagates through the whole coating. Furthermore presence of dispersed phases cover to a brittle behaviour of outer zone and it performs as preferential ways to crack propagation as showed in Fig. 5b.

Radial crack damage, evaluated in terms of number of cracks per millimetre of deformed arc, are evaluated in δ phases of Zn-Sn and Zn-Ti coatings, and in ζ phase in Zn-Sn coatings.

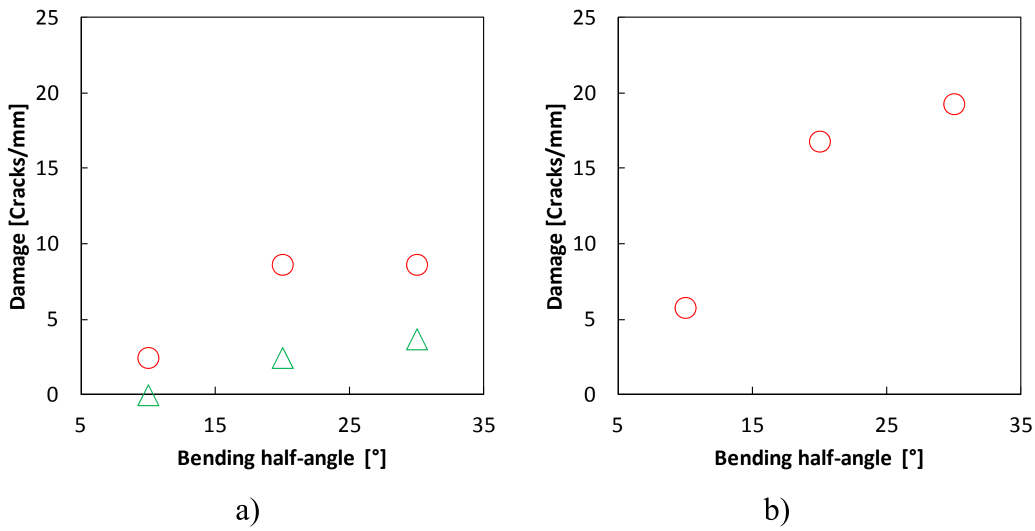



Figure 6: Intermetallic phases damage: a) Zn-Sn3% coating bath, b) Zn-Ti0.5% coating bath.

At low bending angles no cracks are present in ζ phase in Zn-Sn coating, but damage increases at higher angles. In δ phase damage are present al low angles and increase than a plateau at higher deformation angle (Fig. 6a).

But higher damage are present in δ phase of Zn-Ti coatings, where at high deformation angle damage is twice that Zn-Sn coatings.

## CONCLUSION

In this work bending cracks in two Zn-based coatings are investigated in order to evaluate mechanical properties, cracks paths and damage of intermetallic phases.

Presence of Sn do not changes intermetallic phases characteristic in traditional Zn coatings, but presence of Ti leads to a presence of an outer zone, formed by a double phases ductile matrix and a brittle dispessed phase.

Zn-Sn coatings are characterized by high bending strength and good elastic recovery properties than Zn-Ti coatings, probably due to high values of damage.

Presence of brittle dispersed phase, wich behaviour leads to a preferential path to cracks propagate when grains are near δ phase, is the mainly crack mechanism in Zn-Ti coatings.

In Zn-Sn coatings cracks mechanisms are as follows:

- cracks initiate at substrate- δ phase;
- cracks arrest either at δ-ζ interface, in ζ and at ζ-η interface;
- no one cracks initiate in δ or in ζ phases;
- no one cracks are present in η phase in all investigated bending deformation.

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