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# Bending damages in galvanized ductile cast irons

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**Abstract**

Ductile cast irons (DCIs) are characterized by mechanical properties close to low and medium carbon steels. Carbon atoms are mainly localized in graphite nodules, which are dispersed in a metallic matrix. The microstructure of metallic matrix can be ferritic, austenitic, pearlitic, martensitic or their mix, depending on chemical composition and heat treatment. Thanks to the high castability and low production costs, DCIs are used in many fields (e.g., automotive and pipes). The wide utilization of DCIs in many fields and critical application leads to particular attention to the corrosion phenomenon. Hot dip galvanizing is one of most important protection process, used to protect metallic materials (mainly steels) against corrosion in many aggressive environments.
In this work, a ferritic-pearlitic DCI (GS500) was galvanized by using a pure Zn bath at 440°C to generate a zinc coating. Bending tests on galvanized specimen were performed to generate crack damage in the coating phases. The bending cracks path propagation in zinc coatings were observed using both a light optical microscope and scanning electron microscope. A damage parameter, defined as a number of radial crack for a millimeter of the deformed arc, was evaluated for each zinc coating intermetallic phases.


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*Keywords:*Hot Dip Galvanizing; Ductile Cast Iron; Damage; Bending.

## 1. Introduction

Low production costs, good protection and good adhesion to substrate lead to success the zinc-based coatings in many fields. For these reasons, hot dip galvanizing (HDG) is the most important technique to protect a wide class of iron-base alloys against corrosion in many aggressive environments (Vitkova et al. (1996), Katiforis and

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Papadimitriou (1996) and Jintang et al. (2006)).

**Nomenclature**

| | |
|---|---|
| DCI | Ductile Cast Irons |
| HDG | Hot Dip Galvanizing |
| SEM | Scanning Electron Microscope |
| LOM | Light Optical Microscope |

Coating formation is influenced both by physical parameters (e.g., bath temperature, immersion time, pre-galvanizing surface temperature) and by chemical parameters (e.g., chemical compositions, flux chemical composition). The thickness increase of hot dip galvanizing coatings is due mainly to the interdiffusion mechanism of zinc and iron atoms between zinc-based melting and iron-based specimens dipped in the bath.
Due to different chemical composition, the interdiffusion of atoms generates a nonuniform coating. In the outer zone, the coating is rich in zinc whereas in the inner zone the coating is rich in iron. From inner zone to the outer one, the presence of different iron/zinc ratios contents generates different intermetallic phases as shown in the phase diagram (Fig. 1). Therefore, the zinc coating can be considered as a multilayer system meanly formed by four phases, characterized by a different thickness and mechanical properties:

- The outer layer is a ductile η phase with maximum Fe content up to 0.03 wt%.
- The subsequent layer is an isomorphs phase (ζ phase) characterized by 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 (Marder (2000)).
- δ phase is a brittle one, with Fe content up to 11.5 wt% and characterized by a hexagonal crystal structure.
- The inner phase (Γ) is a very thin layer characterized by Fe content up to 29 wt% and by an FCC structure.

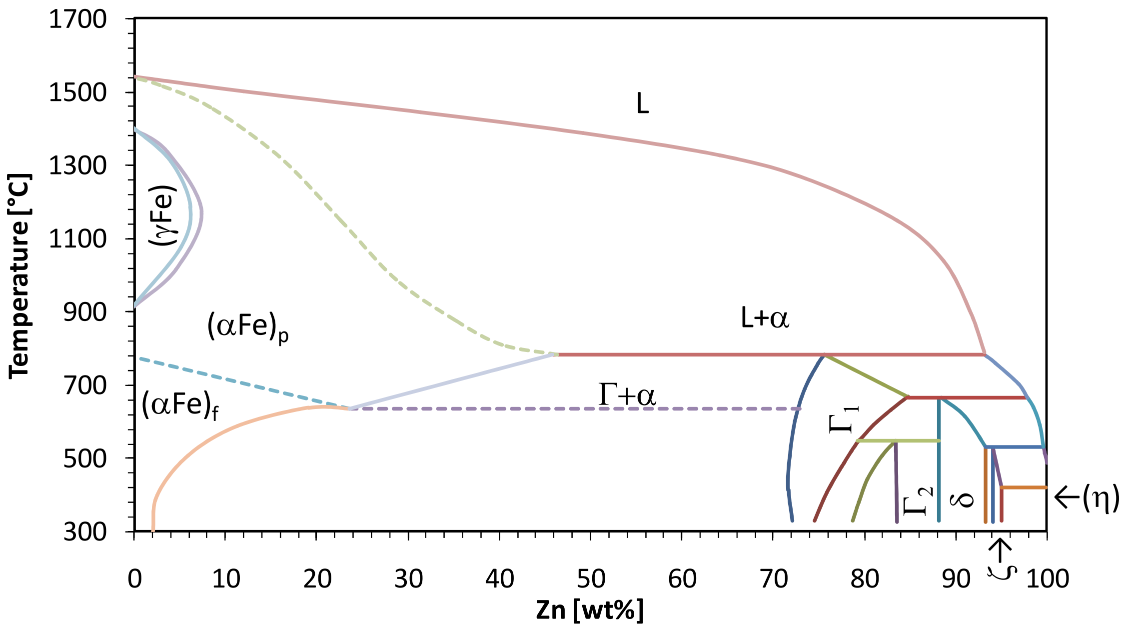



Fig. 1.Zinc-iron phase diagram.

The optimizing of coatings microstructure allows improving coating properties such as substrate adherence, corrosion behavior or simply external aspects, through the addition of alloying elements or different pretreatments.

HDG processes are very important regarding typologies of coatings. 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 (Yoon et al. (2009)). To reduce scraps, the presence of the alloy elements in the bath allows optimizing the HDG processes. Furthermore, the presence of alloying metals allows changing the intermetallic phases usually present in the traditional coatings, improving both mechanical and corrosion properties (Vitkova et al. (1996)). Many authors analyzed the influences of alloy elements either regarding microstructural phases compositions or mechanical properties (Katiforis and Papadimitriou (1996), Jintang et al. (2006) and Marder (2000)).
Analyses performed on electrochemically passivated HDG surface show the presence of stable reaction products that allow improving corrosion resistance (Marder (2000), Yoon et al. (2009), Singh and Glosh (2008) and Evangelos and Papadimitrou (2001)).
The presence of silicon in the coated steel strongly influences coatings formation and their properties. Mechanisms of silicon interaction with galvanizing reactions are the following (Shibli and Manu (2006)):

1) Galvanizing reactions move Fe$\alpha$ toward $\Gamma$ phase;
2) Silicon does not move toward $\Gamma$ phase because its solubility in $\Gamma$ is very low. As consequence silicon increases its contents at Fe$\alpha - \Gamma$ interface;
3) $\alpha$-Fe, reach in silicon, breaks the interface, and particles enter in the $\delta$ phase;
4) Particles dissolving in the $\delta$ phase increases the thickness.

Traditional pre-galvanizing treatment can be optimized by replacing conventional industrial chloride flux with a vegetable oil like the linseed oil. Moreover, it is also possible to use mineral oil. The presence of mineral oil protects the substrate acting as a barrier against oxygen and limiting the galvanization interdiffusion. However, the addition of hydrochloric acid in the oil leads to improvements in coated areas and adherence. Also, the natural fatty acid used in the flux operation leads to good galvanizations due to its light acidity (Balloy et al. (2007)).
Bath chemical composition strongly influences the intermetallic phases growth process. It is known that strontium improves both the adhesive strength and corrosion resistance of hot-dip galvanized coating (Vagge and Raja (2009)). The presence of $SiO_2$:$Na_2O$ molar ratio of silicate solution leads to a decrease of the corrosion current densities and an increase of the polarization resistance and total impedance values, enhancing the corrosion resistance concerning the properties of traditional HDG (Yuan et al. (2010)).
In the outdoor exposition, to prevent the penetration of the aggressive ion Cl-, a presence of oxide under the coating is accepted. Moreover, the presence of ZnO in the inner HDG layer improves corrosion resistance (Shibli and Manu (2006)).
In many cases, painting can be used to increase corrosion resistance. Painting adhesion on the galvanized surface can be improved by using organofunctional silane deposited on hot-dip galvanized cold rolled steels (Bexell and Grehlk (2007)).
It is well known that Pb content fluidizes the zinc bath and increases basal plane texture coefficient. Therefore, $\Gamma$ layer thickness can be increased by increasing the Pb content of the zinc bath. Coatings characterized by good corrosion resistance show high values of basal texture coefficient but smaller $\Gamma$ layer thickness (Asgari et al. (2008)). Many processes were optimized in these terms, but today the presence of Pb cannot be accepted due to recent laws. The main element that is usually considered as Pb substitute is the Sn, but another metallic element can be used leading to different intermetallic phases formations.
Damage of intermetallic phases influences the corrosion resistance. The presence of cracks in the coatings weakens the coating barrier effect (Gallego et al. (2007), Di Cocco and Zortea (2010), Di Cocco et al. (2014), Di Cocco et al. (2017), Iacoviello and Di Cocco (2016) and Di Cocco (2012)).
In this work, the coatings phases formation obtained by pure zinc bath was investigated considering five different dipping time. Mechanical behavior was investigated by performing bending tests. Damage micromechanisms were quantitatively evaluated by means of LOM observations.

## 2. Material and Methods

3 mm thick specimens were cut from a commercial bar. Table 1 shows the DCIs chemical composition.
Bending tests were performed using a non-standard device and they were repeated three times for each considered dipping duration. Tests were performed using an electromechanical 100kN testing machine, considering a crosshead displacement equal to 35 mm that corresponds to a bending half-angle equal to 30°.

In order to identify the damaging mechanisms for each investigated dipping duration and loading conditions, longitudinal sections of the bent specimens were metallographically prepared and observed using both an optical microscope (LOM) and a scanning electron microscope (SEM). The damage level was evaluated in term of "cracks density" defined as the cracks number contained in a millimeter of the deformed arc.

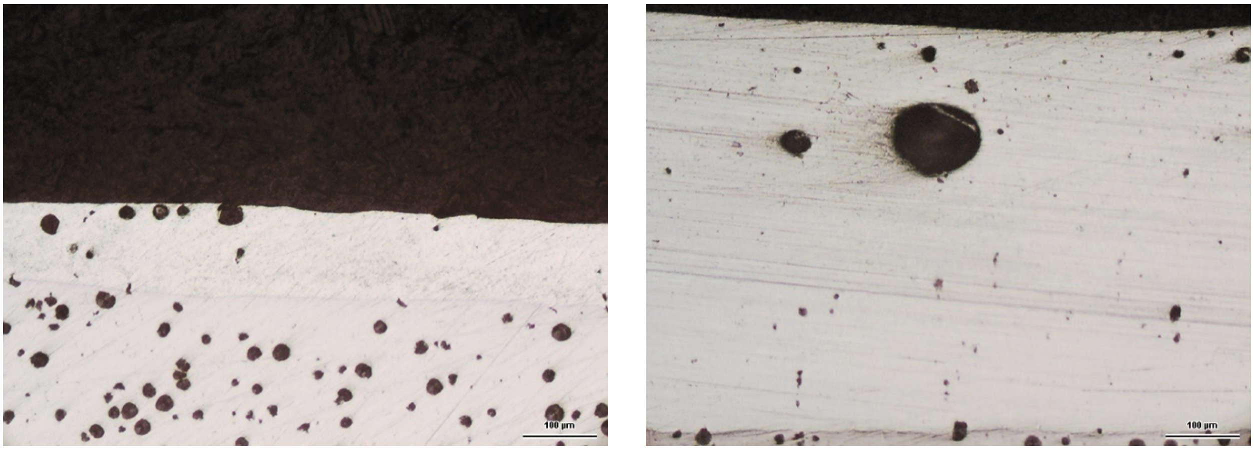
Table 1: Chemical composition investigated DCI (wt%).

| C | Si | Mn | P | S | Cr | Sn | Fe |
|---|---|---|---|---|---|---|---|
| 3.65 | 2.72 | 0.18 | 0.03 | 0.010 | 0.05 | 0.035 | Bal. |

## 3. Results and Discussion

Galvanized DCI specimens were investigated by using LOM observation of the coating sections (Fig. 2). The coatings are characterized by the presence of the traditional intermetallic phases for all the investigated dipping times (an inner δ phase, an intermediate phase ζ and an outer phase η). Furthermore, graphite nodules (embedded in the DCI substrate) are also present in the coatings for all investigated dipping time.

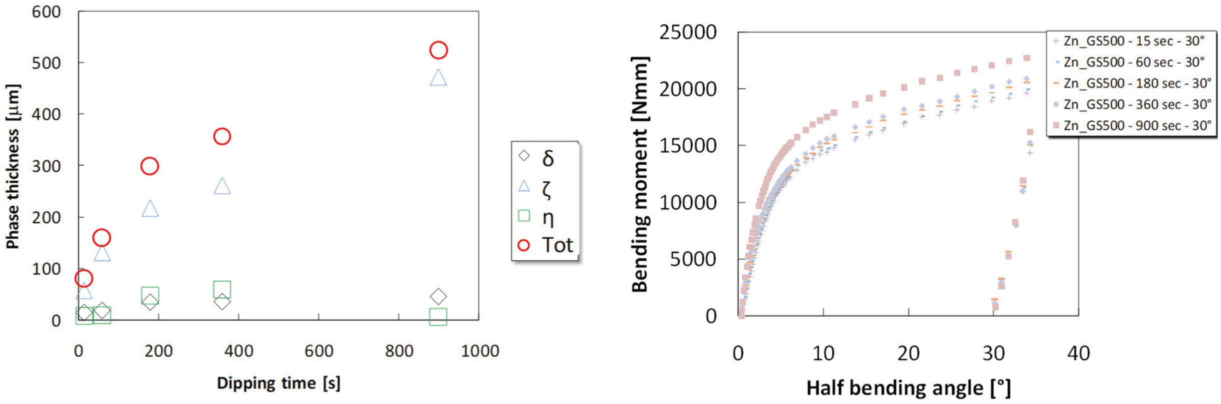
Considering low dipping times, graphite nodules are observed in different positions of coatings in all intermetallic phases (Fig. 2a). For longest dipping times, the nodules seem to be more dispersed in the coating and their diameters range from very small to really large if compared to the "original" nodules embedded in the DCI matrix (Fig. 2b). According to the LOM observations, it is possible to suggest graphite nodules migrate from the DCI to the coating, with the carbon atoms that diffuse obtaining only a few very large nodules.
The thicknesses of other phases (δ and η) are smaller than the thickness of ζ phase, and this is due to high interdiffusion phenomenon of iron in the coating due to high values of silicon in the DCI matrix ("hypersandelin effect").




a) b)

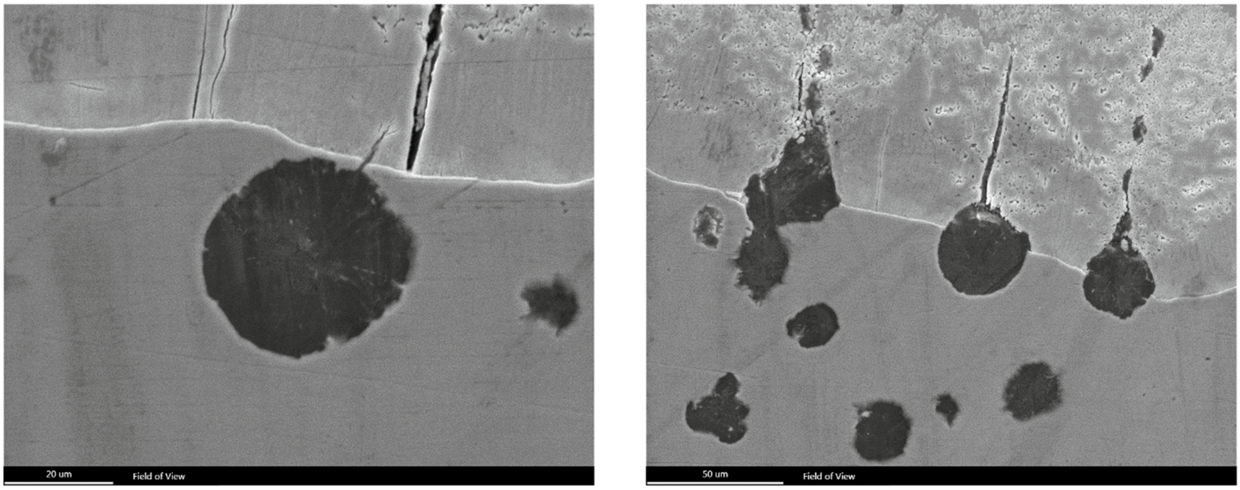
Fig. 2. Section of zinc coatings: a) 15 s, b) 900s.

The results of the bending tests show an increase of the bending moment for longest dipping time as shown in Fig. 3b. This is due to the combined effect of increased thickness of the coating (larger than 0.5 mm) and its different phases composition.
The observations of coating section (Fig. 4 and Fig. 5a) show the presence of radial cracks in the tension side of the bending specimens. Cracks start in the δ phase (the most brittle phase observed in this work), and propagate toward ζ phase, arresting at δ-ζ interface or in ζ phase as also observed in other works focused on hypersandelin steels coatings (Di Cocco et al. (2014) and Di Cocco (2012)).
The evolution of the thicknesses for all the investigated dipping time is shown in Fig. 3a, where the total thickness follows a typical diffusion law. The ζ phase is the main intermetallic component for all investigated dipping times.



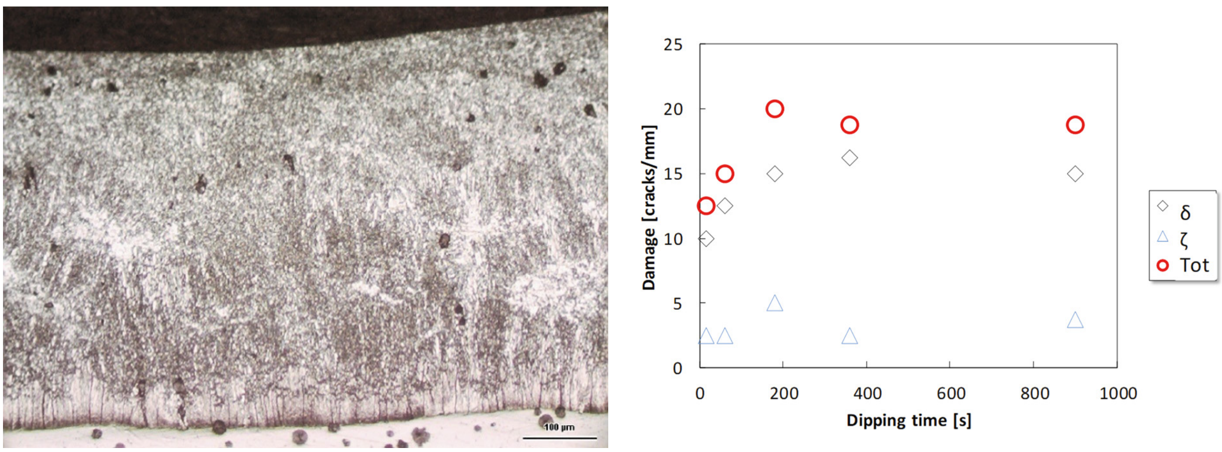

a) b)

Fig. 3. Coatings specimens: a) coating and intermetallic phases thicknesses, b) bending behavior.




a) b)

Fig. 4. Coating cracks SEM observations: a) crack induced by nodules graphite in DCI, b) cracks induced by graphite nodules at DCI-Coating interface




a) b)

Fig. 5. Coating damage: a) radial cracks in coating obtained from 900s of dipping time, b) damage-dipping time evolution.

Focusing the tension side, the presence of graphite nodules generates more radial cracks starting from external nodules. In particular, nodules in DCI matrix in the proximity of DCI-coating interface generate cracks in DCI substrate, which propagate in δ phase arresting inside this phase (Fig. 4a). Other nodules positioned across DCI and δ phase are characterized by an onion crack also observed in other works (e.g., Iacoviello and Di Cocco (2016)) (Fig. 4b). In this case, radial cracks start from nodules and propagate in δ and arrest at the δ-ζ interface or in ζ phase.
Considering the number of radial cracks/mm of deformed arc as damage parameter (Fig. 5a), the quantification of damage (Fig. 5b) indicates an increase of damage in δ phase up to a dipping time of 360 s and a "quasi-uniform" damage in δ phase for 15, 60 and 360 s. Finally, considering the total amount of the crack density both in δ and in ζ phases, it is possible to underline that the maximum damage is obtained for a dipping time of 180 s (Fig. 5b).

## 4. Conclusion

In this work, a ferritic-pearlitic DCI was zinc coated using a hot dip galvanizing procedure. Coatings obtained for different dipping times (15, 60, 180, 360 and 900s) were analyzed using LOM observations. The coating and intermetallic phases thicknesses for the different dipping times measured indicate a high DCI reactivity, due to high silicon content in the DCI. In addition, it was observed the presence of graphite nodules in the coatings.
The bending behavior showed a strong dependence of bending moment on the coating thickness (higher than 0.5mm after a dipping time of 900 s).
The damage analyses were performed by means SEM and LOM observations of coating sections. In this case, in tensile sides of bent specimens, the presence of radial cracks was observed. Many cracks initiated at the DCI-δ interfaces, as in traditional bent coatings, but the presence of graphite nodules imply the cracks initiation also corresponding to these graphite elements, with cracks that propagate both in DCI matrix and in δ phase.
Considering the cracks density (number of cracks in one millimeter of deformed arc) as damage parameter, the worst condition is obtained at 180 s of dipping time.

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