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# Analysis of the Al and Ti additions influences on phases generation and damage in a hot dip galvanizing process

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## Abstract

Cheap iron-based alloys, such as Ductile Cast Irons (DCIs) and low carbon steels, are more and more used in the mechanical field because they are characterized by good strength and good workability. However, the low value of electrochemical potential of low carbon steel leads to quick environmental corrosion that can compromise the operative life of mechanical components. Therefore, it is important to protect them against corrosion even for safety and reliability reasons. The use of a traditional protection technique, like Hot Dip Galvanizing (HDG), allows low costs too. In this work, the phase formation during HDG process is presented and discussed. In particular, the influence of Al and Ti additions on the pure Zn bath is shown in the metallographic analysis, presenting also the results of pure Zn bath.

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## 1. Introduction

Among protection techniques suitable against corrosion, the most employed is Hot Dip Galvanizing (HDG), Opbroek et al. (1995). This technique is valuable since it has a twofold action: first of all it consists in a barrier that isolates the metal from the aggressive environment, secondly the zinc in the coating has an electrochemical potential lower than that of the iron; therefore, the substrate is protected by the Zn-based coating also if this latter is damaged:

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the Zn corrosion products that arise due to the electrochemical conditions are able to restore the local damage in the barrier, as stated by Bellini and Carlino (2019).

According to Marder (2000), HDG has been employed for many years, but only in the last time higher mechanical characteristics and corrosion resistance have been demanded. Therefore, innovative techniques have been introduced for producing special Zn-based coatings with both conventional and advanced intermetallic phases. The differences between the innovative HDG processes and the conventional ones are very little and consist in adjustments employed to cut the production expenses, Urednicek et al. (1987). In fact, the advanced techniques can be adopted in the conventional industrial plants too by simply substituting a few pieces of the process line equipment.

Interdiffusion between Fe and Zn atoms is at the base of HDG coatings, and it is suitable for producing a film with an altered chemical structure. In fact, various intermetallic phases can be present in coatings, as witnessed in the Zn-Fe phases diagram. Moreover, the presence in the bath of other elements makes the corresponding diagram change, and the intermetallic phases produced by the HDG method influence the characteristic properties of Zn-based coatings.

Many chemical Zn bath compositions are studied in the current research activities, because the request for new Zn-based coatings, characterized by various intermetallic phases and presenting optimized mechanical behaviour, is increasing. Vantadori et al. (2017) and Carpinteri et al. (2016) have recently studied the effects of two dissimilar types of enhanced Zn-based coatings on the structural characteristics of ipersandelin steel plates, and they have introduced a new mechanical model, suitable for the estimation of the bending behaviour of these plates knowing only the coatings composition, their intermetallic phases and their structural characteristics.

During bending of flat plates, the damage micromechanisms can be detected in the intermetallic phases; in fact, radial cracks generate in inner phases, that are fragile, and then they spread towards the coating surface. It is worth to note that the radial cracks generated in under tension coating are blocked by the different mechanical response of the various intermetallic phases, Shah et al. (1992). On the contrary, in the under compression coating the cracks are absent; however, damages can arise in brittle phases, in the form of boundary delamination induced by high thickness, as found by Cape et al. (1998) and Natali et al. (2014).

The mechanical behaviour of both the whole coating and the various phases can be investigated by analysing the crack development inside the material. For example, in the last years the ductile cast iron is more and more investigated, since it possesses structural characteristics similar to those of the conventional low and medium carbon steel. In literature several studies, such Cavallini et al. (2013), Cavallini et al. (2016) and Iacoviello et al. (2019) analysed the damage mechanism of carbon nodules present in this material, and recently the performance of protective coatings applied on parts made of ductile cast iron is explored in view of producing safer components.

Finally, some investigations have been carried out for varying the colour of Zn-based coatings by means of Al, as Osinski et al. (1983), Chen et al. (1990), Willis et al. (1989) and Perrot et al. (1992), or Ti additions in the galvanizing bath. This possibility finds application in the civil construction field; in fact, in such field, the coatings accomplish a double task: firstly, it constitutes the protective barrier against corrosion, secondly, it gives a pleasant appearance to surfaces without the need for a further painting operation.

## 2. Material and methods

An ipersandelin low carbon steel, characterized by the chemical composition shown in Table 1, was used to prepare flat rectangular specimens.

Table 1. Chemical composition of the specimen steel.

C	Si	Mn	P	Mo	Cr	Al	Fe
0.06	0.014	0.332	0.005	0.0064	0.025	0.0309	Bal.

Each specimen was prepared by an appropriate cleaning process which was composed of 2 main phases. In the first one, there was a cleaning phase able to eliminate the fatty impurity on the surface, by using a solution containing

tension-active elements; in the second one, there was another cleaning phase, able to eliminate any oxide on the surface. For this operation an acid was used in the solution, containing 20% sulfuric acid at 50 °C.

Then the specimens were galvanizing by using three different zinc-based baths; the first one was a pure Zn bath, the second one was obtained by additions of 5%Al and the third one was obtained by the pure Zn bath too, by additions of 1.0% Ti. For all the baths, a dipping time of 900 s was considered in order to better develop the intermetallic phases.

The analyses of intermetallic phases and their damage were performed by means of a light optical microscope, after traditional metallographic preparation of coatings sections.

### 3. Experimental results

Altering the chemical composition of the galvanizing bath is the most employed solution to modify the Zn coating process.

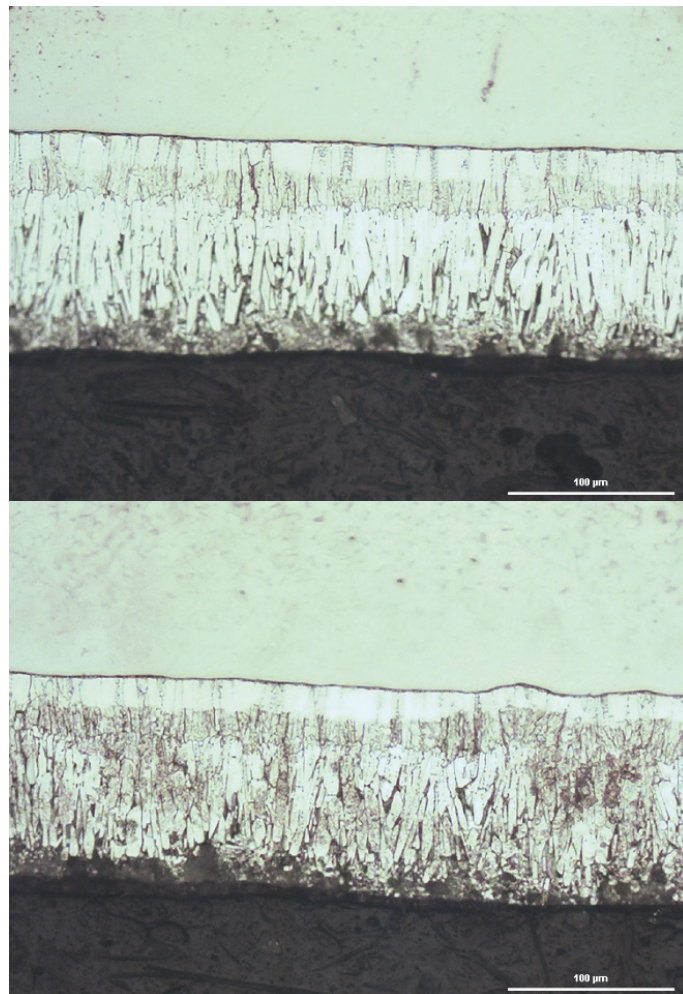


Fig. 1. Pure zinc bath microstructure (two different points on coating section).

Various intermetallic phases can be generated by including several metallic elements in the pure Zn bath. As visible in Fig. 1, four intermetallic phases can be usually found in coatings produced by a pure Zn bath:

- the  $\Gamma$  phase (0.001% vol), which is composed of a very thin film, with a thickness of a few atoms;
- the  $\delta$  phase (2% vol), with a compacted morphology;
- the  $\zeta$  phase (64%vol), whose morphology is columnar;
- the external  $\eta$  phase (33.999% vol), produced by Zn wet liquid solidification.

A light coating can be produced by adding Al, as visible in Fig. 2. A eutectic Zn-Al phase distinguishes this coating, presenting a lamellar morphology as well as pearlite. In this coating, the  $\sigma$  phase volumetric content is 16%, while the lamellar phase content is 84%.



Fig. 2. Zn - Al 5 wt% bath microstructure (two different points on coating section).

Instead, many phases are formed by adding a low quantity of Ti, the 1wt%, in the Zn bath. As visible in Fig. 3, there was the development of a conventional  $\delta$  phase together with a new phase, called  $\tau$  phase, that is rich in Fe and Ti and its hardness is very high. This phase could be distributed in both a  $\zeta$  phase and a  $\eta$  phase. Occasionally, the presence of a local eutectic or eutectoid chemical composition could generate a lamellar phase in the external zone of the coating. In the studied case, the lamellar phase volumetric content was 38%, the compact one is 29%, the  $\delta$  one was 5% and the  $\tau$  one was 28%.



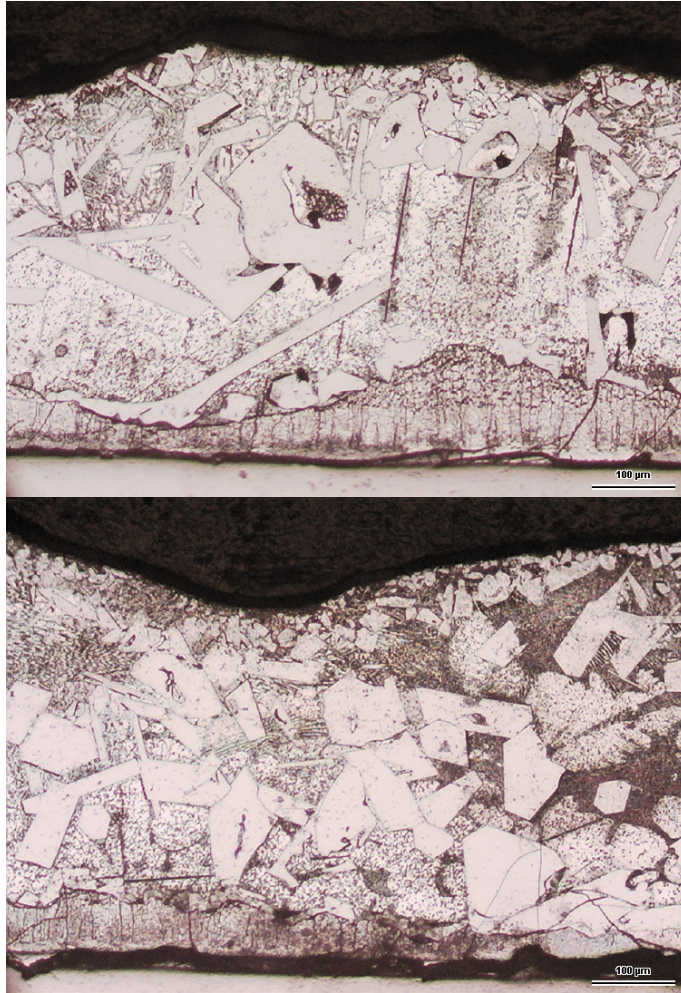


Fig. 3. Zn - Ti 1.0 wt% bath microstructure (two different points on coating section).

For both the pure Zn coating and the 1.0%Ti coating, the presence of brittle phases, Di Cocco (2012), respectively  $\delta$  and  $\sigma$ , was characterized by closed radial cracks, probably due to the thermic dilatation effects. These cracks propagated in the  $\delta$  phase up to the  $\delta$ - $\zeta$  interface, instead in the  $\sigma$  phase the thermal cracks can arrest or at  $\sigma$ -compact phase interface or in the  $\sigma$  phase. Furthermore, in the 1.0%Ti many longitudinal cracks were observed in the  $\sigma$  phase, indicating partial delamination of the coating. No cracks were observed in the 5%Al coatings phases.

#### 4. Conclusions

The relationship between the coating mechanical characteristics and the Hot Dip Galvanizing process parameters can be comprehended analysing the kinetics of the coating developments. In fact, the mechanical characteristics can be deeply modified by the intermetallic phases, as shown in the work of Vantadori et al. (2017). For this reason, the supervision of the phases present in the coating composition is needed for mechanical properties enhancement. In the scientific literature, there are a few models that consider the kinetics development of intermetallic phases. Taking into consideration both the interdiffusion phenomena between zinc and iron atoms and the phases stability for precise chemical composition is substantial for anticipating the thickness of the phase.

Cracks formation and propagation can be anticipated through a damage model, that should be developed by analysing the damage micromechanisms of intermetallic phases. The mechanical characteristics of coated parts can be calculated by means of a model, taking into account the damage micromechanisms and the phases formations kinetics.

In this work, the Hot Dip Galvanizing process was applied on specimens made of ipersandlin low carbon steel, considering different bath composition. Then, the obtained coatings were analysed by optical microscopy, finding the formation of different intermetallic phases, depending on the bath composition.

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